



(11) Publication number : **0 615 158 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **94301571.9**

(51) Int. Cl.⁵ : **G03C 1/053, G03C 1/76,
G03C 1/89**

(22) Date of filing : **04.03.94**

(30) Priority : **04.03.93 JP 43865/93**

(43) Date of publication of application :
14.09.94 Bulletin 94/37

(84) Designated Contracting States :
DE GB NL

(71) Applicant : **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome
Shinjuku-ku
Tokyo 163 (JP)

(72) Inventor : **Morita, Kiyokazu**
c/o Konica Corporation,
1 Sakura-machi
Hino-shi, Tokyo (JP)
Inventor : **Tachibana, Noriki**
c/o Konica Corporation,
1 Sakura-machi
Hino-shi, Tokyo (JP)

(74) Representative : **Ellis-Jones, Patrick George**
Armine
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **A silver halide photographic light-sensitive material.**

(57) A silver halide photographic light-sensitive material is disclosed. The light-sensitive material comprises a support having thereon a silver halide emulsion and optionally a hydrophilic colloid layer other than the emulsion layer. At least one of these layers contains a latex of polymer comprising a repeating unit derived from a monomer having a solubility in water of not higher than 0.025 % by weight at 25°C and the content of said repeating unit in said polymer is not less than 50 % by weight.

EP 0 615 158 A1

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material, and more particularly to a silver halide photographic light-sensitive material whose layer physical properties are improved without affecting its photographic characteristics.

BACKGROUND OF THE INVENTION

Generally speaking, the hydrophilic colloid layer of a silver halide photographic light-sensitive material is required not only to have no bad influence upon its photographic characteristics but also to have a necessary performance for its layer physical/antistatic properties. Therefore, various attempts have conventionally been made, when coating on a support a hydrophilic colloid layer such as a silver halide emulsion layer, an interlayer or a protective layer, to improve the hydrophilic colloid layer's physical properties such as dimensional stability, scratch resistance, elasticity, pressure resistance and drying characteristic in the manner of incorporating a polymer latex formed by polymerization of various monomers into the hydrophilic colloid layer; and other attempts to improve the antistatic characteristics of the hydrophilic colloid layer by preventing the phenomenon called static marks, appearing in the form of spots or branched or feather-like marks when the light-sensitive emulsion layer is exposed to discharge of static electricity having accumulated and then processed, in the manner of dispersing the accumulated static charge by adding a surfactant to the surface of the hydrophilic colloid layer.

From the above point of view, there have heretofore been proposed the use of a latex of polyvinyl acetate in U.S. Patent No. 2,376,005; the use of a latex of a polyalkyl acrylate in U.S. Patent No. 3,325,286; the use of latexes of polymers of n-butyl acrylate, ethyl acrylate, styrene, butadiene, vinyl acetate and acrylonitril in Japanese Patent Examined Publication (hereinafter abbreviated to JP E.P.) No. 5331/1970; the use of latexes of polymers of an alkyl acrylate, acrylic acid and sulfoalkyl acrylate in JP E.P. No. 22506/1971; the use of polymer latexes containing 2-acrylamido-2-methylpropanesulfonic acid in Japanese Patent Publication Open to Public Inspection (hereinafter abbreviated to JP O.P.I.) No. 130217/1976; the use of the anionic, betaine and cationic activators described in U.S. Patent Nos. 3,082,123, 3,201,251, 3,519,561 and 3,625,695, West German Patent Nos. 1,552,408 and 1,597,472, JP O.P.I. Nos. 85826/1974, 129623/1978, 159223/1979 and 19213/1973, and JP E.P. Nos. 39312/1971, 11567/1974, 46775/1976 and 14417/1980; and the nonionic surfactants described in JP O.P.I. No. 80023/1977, West German Patent Nos. 1,422,809 and 1,422,818, and Australian Patent No. 54,441/1959.

However, the use of a polymer latex, particularly the combined use of it with an activator, seriously affects photographic characteristics, causing, for example, desensitization of the silver halide emulsion, devitrification in development, dye stain after development, degradation of the halftone quality in graphic arts film, generation of static marks on medical X-ray film. In order to solve the above problems, U.S. Patent Nos. 3,525,620, 3,323,286 and 3,142,568, Belgian Patent Nos. 768,558 and 708,347, German Patent No. 2,047,150, British Patent No. 1,498,697, and JP O.P.I. No. 50967/1982 propose techniques that use polymer latexes with specific surfactants, but such techniques are applicable to only limited kinds of emulsions, and none of them have no effect upon the fogging, developing and antistatic characteristics of the light-sensitive material.

JP O.P.I. Nos. 50240/1980, 52882/1973 and 52883/1973, and JP E.P. Nos. 47371/1980 and 19772/1979 describe techniques that use a polymer latex obtained by using a water-soluble high-molecular material at the time of its polymerization. Such techniques, although useful for improving photographic characteristics, are not enough for improving physical properties, and leave the problems of devitrification, viscosity increase in coating, deterioration of scratch resistance and deterioration of antistatic characteristics, so that the polymer latex can not be used in a sufficient amount.

JP O.P.I. No. 135335/1990 discloses a technique to use a methacrylic acid polymer, but its improving effect is insufficient and it largely affects the antistatic characteristics of the light-sensitive material.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an excellent silver halide photographic light-sensitive material whose physical and antistatic properties are improved without adversely affecting its photographic characteristics.

It is another object of the invention to provide a silver halide photographic light-sensitive material free from any coating trouble.

The objects of the invention are accomplished by a silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer and optionally a hydrophilic colloid layer, in which

at least one of the silver halide emulsion layer and hydrophilic colloid layer contains a latex of polymer comprising a repeating unit derived from a monomer having a solubility in water at 25°C of not higher than 0.025% by weight. The content of the repeating unit derived from a monomer having a solubility in water at 25°C of not higher than 0.025% by weight in the polymer is not less than 50% by weight of the polymer of latex.

5

DETAILED DESCRIPTION OF THE INVENTION

The above monomer is preferably an acrylate compound, and more preferably an acrylate compound used in combination with a methacrylate compound. The number average particle size of the polymer latex of the invention is preferably not more than 300nm.

The polymerization of the polymer latex of the invention is preferably carried out in the presence of a water-soluble polymer and/or a surfactant.

At least one of the monomers for use in forming the polymer latex of the invention has a solubility in water at 25°C of preferably not more than 0.025% by weight, and more preferably not more than 0.015% by weight. Examples of such the ethylenic monomer include acrylates such as hexyl acrylate, 2-ethyl-hexyl acrylate, octyl acrylate, tert-octyl acrylate, nonyl acrylate, iso-nonyl acrylate, cyclohexyl acrylate, n-stearyl acrylate, lauryl acrylate and tridecyl acrylate; methacrylates such as hexyl methacrylate, 2-ethyl-hexyl methacrylate, octyl methacrylate, iso-octyl methacrylate, tert-octyl methacrylate, nonyl methacrylate, iso-nonyl methacrylate, cyclohexyl methacrylate, n-stearyl methacrylate, lauryl methacrylate and tridecyl methacrylate; and divinylbenzene.

The solubility in water at 25°C of the monomer for use in forming the latex of the invention can be measured according to the method described in the 'Shin Jikken Kagaku Koza, Kihon Sosa 1, p.223-250' ('New Experimental Chemistry Course: Basic Operations 1') (Maruzene Kagaku, 1975). When measured according to this method, the solubility in water at 25°C of, e.g., 2-ethyl-hexyl acrylate is 0.01% by weight, 2-ethyl-hexyl methacrylate 0.005 by weight, cyclohexyl methacrylate 0.00% by weight, whereas in the case of comparative monomers, styrene 0.03% by weight, butyl acrylate 0.32% by weight and butyl methacrylate 0.03% by weight.

For the polymer latex used in the invention, copolymerization of the above monomer compound with different other monomer compounds may be carried out. In this case, it is preferable that the content of repeating unit derived from the monomer, having a solubility in water at 25°C of not larger than 0.025% by weight, in the polymer be not lower than 50%. Examples of copolymerizable ethylenic monomer compounds with the above monomer compounds of the invention include acrylates, methacrylates, vinyl esters, olefins, styrenes, crotonic acid esters, itaconic acid diesters, maleic acid diesters, fumaric acid diesters, acrylamides, acryl compounds, vinyl ethers, vinyl ketones, vinyl heterocyclic compounds, glycidyl esters, unsaturated nitriles, polyfunctional monomers, and various unsaturated acids. From the above compounds one or two or more are selected to be used in combination as monomers for copolymerization.

To show these monomer compounds further in detail, examples of the acrylate include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, tert-butyl acrylate, amyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 2-hydroxyethyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxy acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, ω -methoxypolyethylene-glycol acrylate (addition molar number $n = 9$), 1-bromo-2-methoxyethyl acrylate and 1,1-dichloro-2-ethoxyethyl acrylate.

Examples of the methacrylate include methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, amyl methacrylate, chlorobenzyl methacrylate, sulfopropyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, phenyl methacrylate, cresyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, triethyleneglycol monomethacrylate, dipropylene-glycol monomethacrylate, 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate, 2-acetoxyethyl methacrylate, 2-acetoacetoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-iso-propoxyethyl methacrylate, 2-butoxyethyl methacrylate, 2-(2-methoxyethoxy)ethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, 2-(2-butoxyethoxy)ethyl methacrylate, ω -methoxypolyethylene-glycol methacrylate (addition molar number $n = 6$), allyl methacrylate and dimethylaminoethylmethyl methacrylate chloride.

Examples of the vinyl ester include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl caproate, vinyl chloroacetate, vinylmethoxy acetate, vinylphenyl acetate, vinyl benzoate and vinyl salicylate.

Examples of the olefin include dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, vinyl chloride, vinylidene chloride, isoprene, chloroprene, butadiene and 2,3-dimethylbutadiene.

Examples of the styrene include styrene, methylstyrene, trimethylstyrene, ethylstyrene, chloromethylstyrene, methoxystyrene, acetoxystyrene, chlorostyrene, bromostyrene, trifluorostyrene and vinylmethyl benzoate.

Examples of the crotonic acid ester include butyl crotonate.

5 Examples of the itaconic acid diester include dimethyl itaconate, diethyl itaconate and dibutyl itaconate.

Examples of the maleic acid diester include diethyl maleate, dimethyl maleate and dibutyl maleate.

Examples of the fumaric acid diester include diethyl fumarate, dimethyl fumarate and dibutyl fumarate.

10 Examples of the acrylamide include acrylamide, methylacrylamide, ethylacrylamide, propylacrylamide, butylacrylamide, tert-butylacrylamide, cyclohexylacrylamide, benzylacrylamide, hydroxymethylacrylamide, methoxyethylacrylamide, dimethylaminoethylacrylamide, phenylacrylamide, dimethylacrylamide, diethylacrylamide, β -cyanoethylacrylamide and N-(2-acetacetoxyethyl)acrylamide.

15 Examples of the methacrylamide include methacrylamide, methylmethacrylamide, ethylmethacrylamide, propylmethacrylamide, butylmethacrylamide, tert-butylmethacrylamide, cyclohexylmethacrylamide, benzylmethacrylamide, hydroxymethylmethacrylamide, methoxyethylmethacrylamide, dimethylaminoethylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, diethylmethacrylamide, β -cyanoethylmethacrylamide and N-(2-acetacetoxyethyl)methacrylamide.

Examples of the allyl compound include allyl acetate, allyl caproate, allyl laurate and allyl benzoate.

Examples of the vinyl ether include methylvinyl ether, butylvinyl ether, hexylvinyl ether, methoxyethylvinyl ether and dimethylaminoethylvinyl ether.

20 Examples of the vinyl ketone include methylvinyl ketone, phenylvinyl ketone and methoxyethylvinyl ketone.

Examples of the vinyl-heterocyclic compound include vinylpyridine, N-vinyl-imidazole, N-vinyl-oxazolidone, N-vinyl-triazole, N-vinyl-pyrrolidone.

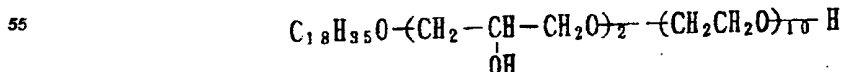
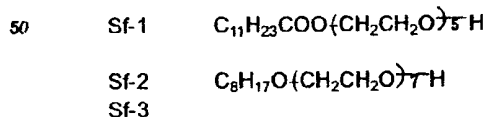
Examples of the glycidyl ester include glycidyl acrylate and glycidyl methacrylate.

25 Examples of the unsaturated nitrile include acrylonitrile and methacrylonitrile. Those of the polyfunctional monomer include divinylbenzene, methylenebisacrylamide and ethyleneglycol dimethacrylate.

Further, acrylic acid, methacrylic acid, itaconic acid, maleic acid; monoalkyl itaconates such as monomethyl itaconate, monoethyl itaconate and monobutyl itaconate; monoalkyl maleates such as monomethyl maleate, monoethyl maleate and monobutyl maleate; citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid; acryloyloxyalkylsulfonic acids such as acryloyloxyethylsulfonic acid and acryloyloxypropylsulfonic acid; methacryloyloxyalkylsulfonic acids such as methacryloyloxydimethylsulfonic acid, methacryloyloxyethylsulfonic acid and methacryloyloxypropylsulfonic acid; acrylamidoalkylsulfonic acids such as 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutanesulfonic acid; methacrylamidoalkylsulfonic acids such as 2-methacrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylbutanesulfonic acid and 2-methacrylamido-2-methylpropanesulfonic acid; and 3-acryloyloxypropyl-2-phosphate; 35 methacryloyloxyalkyl phosphates such as methacryloyloxyethyl phosphate and 3-methacryloyloxypropyl-2-phosphate; and naphthyl 3-allyloxy-2-hydroxypropanesulfonate having two hydrophilic groups. These acids may be used in the form of salts of alkali metals such as Na, K or of ammonium ions. As still further monomer compounds there may be used those crosslinking monomers as described in U.S. Patent Nos. 3,459,790, 3,438,708, 3,554,987, 4,215,195 and 4,247,673, and JP O.P.I. No. 205735/1982. Examples of the crosslinking 40 monomer include N-(2-acetacetoxyethyl)acrylamide and N-(2-(2-acetacetoxyethoxy) ethyl)acrylamide.

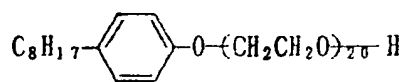
The suitably usable among the above monomers compounds are acrylic acid esters, methacrylic acid esters, vinyl esters, styrenes and olefins.

45 Surfactants usable in the invention may be any of anionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants, and are preferably anionic and/or nonionic surfactants. As the anionic surfactants and/or nonionic surfactants, various compounds known to those skilled in the art may be used, but particularly, anionic surfactants are preferred. The following are useful examples of the surfactant for the invention.



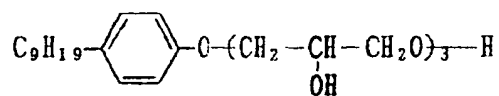
Sf-4

5



Sf-5

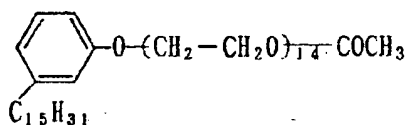
10



15

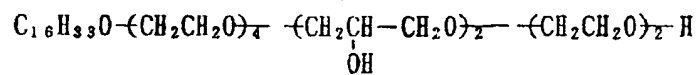
Sf-6

20



25

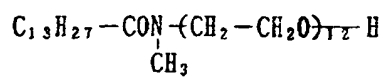
Sf-7



30

Sf-8

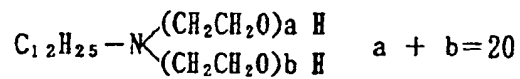
35



40

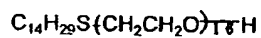
Sf-9

45



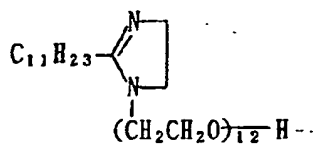
Sf-10

Sf-11

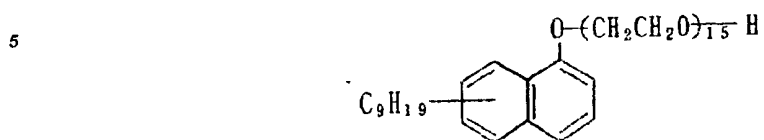


50

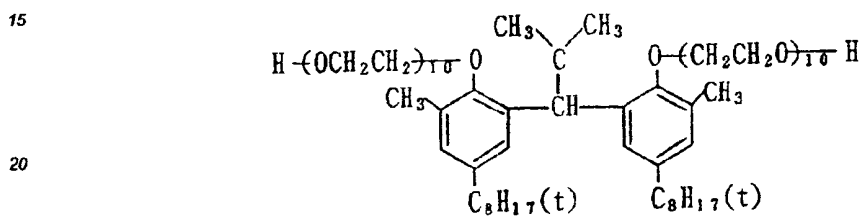
55



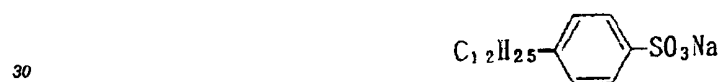
Sf-12



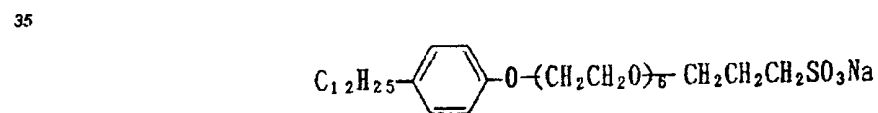
Sf-13



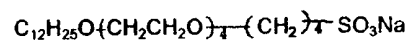
25 Sf-14



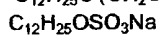
Sf-15



Sf-16



Sf-17



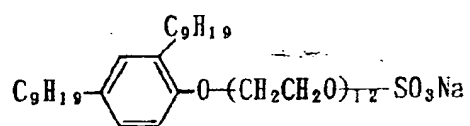
Sf-18

45



Sf-19

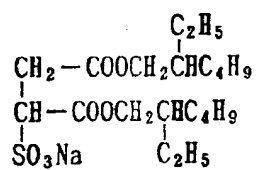
5



10

Sf-20

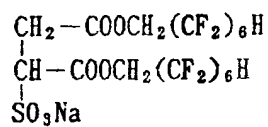
15



20

Sf-21

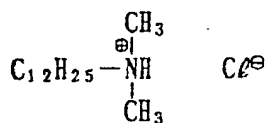
25



30

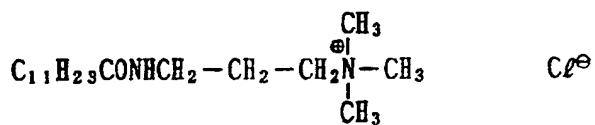
Sf-22

35



Sf-23

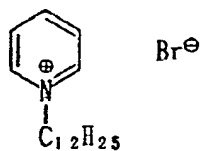
40



45

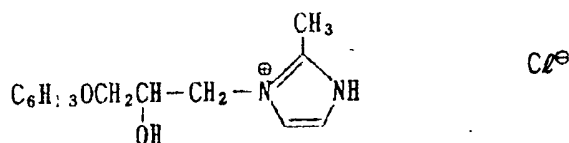
Sf-24

50

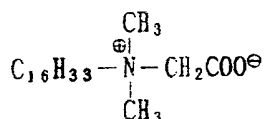


55

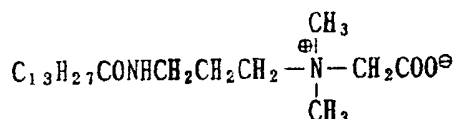
Sf-25



Sf-26



Sf-27



The water-soluble high molecular material preferably used for the invention includes synthetic water-soluble polymer materials and natural water-soluble polymer materials; either may be suitably used in the invention. Of these the synthetic water-soluble polymer materials include ones having a nonionic group, ones having an anionic group, ones having a cationic group, ones having both nonionic and anionic groups, ones having both nonionic and cationic groups, and ones having both anionic and cationic groups in their respective molecular structures. The nonionic group includes an ether group, an alkyleneoxide group, a hydroxy group, an amido group and an amino group. The anionic group includes a carboxyl group and its salts, a phospho group and its salts, a sulfo group and its salts. The cationic group includes a quaternary ammonium salt group and a tertiary amino group.

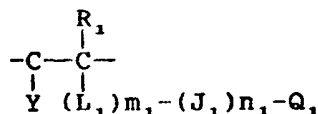
The natural water-soluble polymer materials also include ones having a nonionic group, ones having an anionic group, ones having cationic group, ones having both nonionic and anionic groups, ones having both nonionic and cationic groups and ones having both anionic and cationic groups in their respective molecular structures.

As the water-soluble polymer, either synthetic or natural, any of those having an anionic group or both non-ionic and anionic groups may be suitably used.

In the invention, the water-soluble polymer is one having a solubility of preferably not less than 0.05g, and more preferably not less than 0.1g in 100g of water at 20°C.

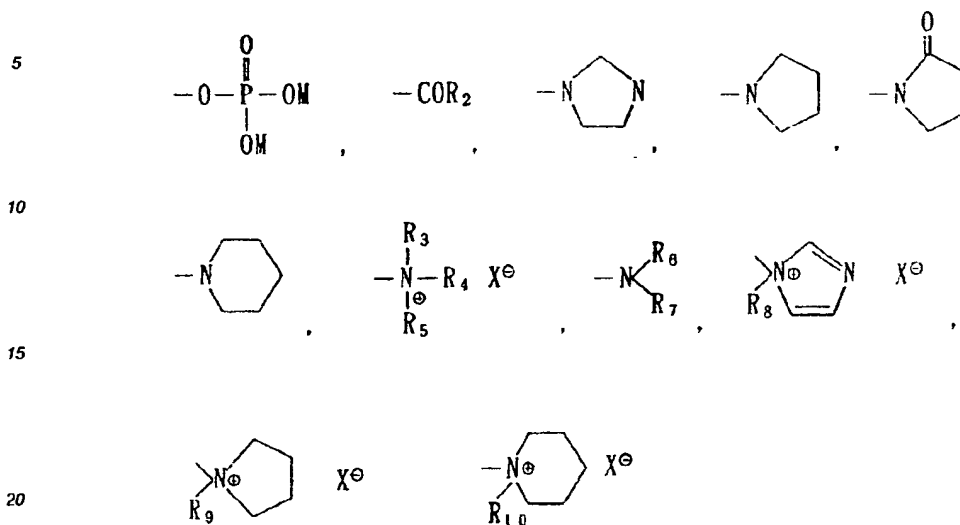
The synthetic water-soluble polymer includes those containing repeating units represented by the following Formula (1) and/or Formula (2) in a ratio of to to 100 mol% per polymer molecule thereof.

Formula (1)



wherein R₁ represents a hydrogen atom, an alkyl group, a halogen atom or a -CH₂COOM group, and preferably an alkyl group having 1 to 4 carbon atoms; L₁ represents a divalent linkage group such as -CONH-, -NHCO-, -COO-, -OCO-, -CO- or -O-; J is an alkylene group, an arylene group or an oxyalkylene group; and Q₁ repre-

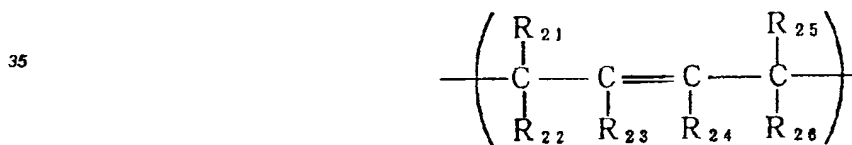
sents -OM, -NH₂, -SO₃M, -COOM,



a hydrogen atom or R_3 . Out of these, $-COOM$ and $-SO_3$ are preferred, particularly $-SO_3M$ is most suitably usable.

25 M represents a hydrogen atom or a cation (such as an alkali metal ion, an ammonium ion); R₃, R₄, R₅, R₆, R₇, R₈, R₉ and R₁₀ each represent an alkyl group having 1 to 20 carbon atoms; X represents an anion; m₁ and n₁ each represent an integer of 0 or 1; and Y represents a hydrogen atom or -(L₂)m₂-(J₂)n₂-Q₂, wherein L₂, J₂, Q₂, m₂ and n₂ are the same as defined for L₁, J₁, m₁ and n₁, respectively.

Formula (2)

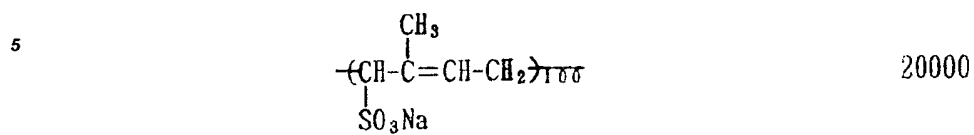


40 wherein R₂₁, R₂₂, R₂₃, R₂₄, R₂₅ and R₂₆ each represent a hydrogen atom, an alkyl group having 1 to 8 carbon atoms or an aryl group having 6 to 20 carbon atoms or a -SO₃X group, wherein X is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, an ammonium group or an amino group; provided at least one of R₂₁, R₂₂, R₂₃, R₂₄, R₂₅ and R₂₆ is -SO₃X.

45 Examples of the synthetic water-soluble polymers represented by Formulas (1) and (2) are listed below, in which each suffixed number represents the content percentage of each monomer unit.

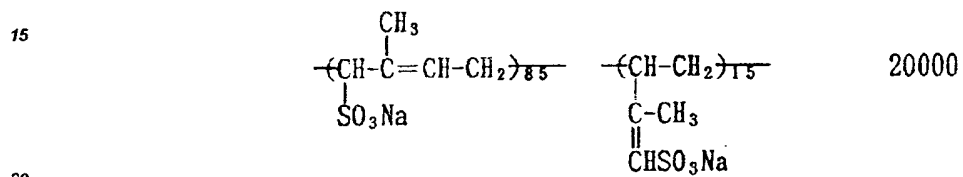
P - 1	Number average molecular weight
	M_n
$\text{-(CH-}\overset{\text{CH}_3}{\underset{\text{SO}_3\text{Na}}{\text{C}}}=\text{CH-CH}_2\text{)-}_{100}$	5000

P - 2

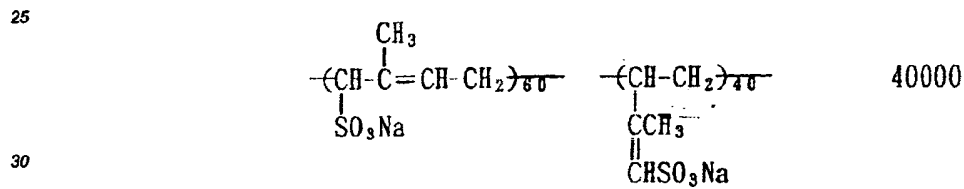


10

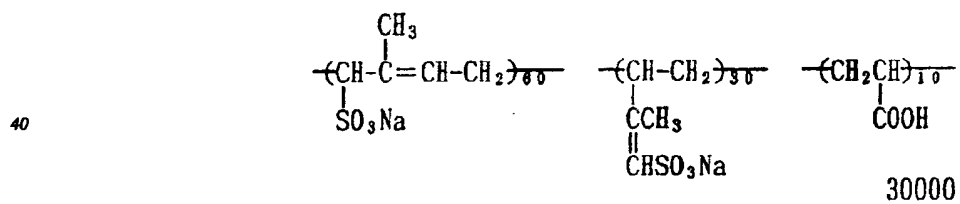
P - 3



P - 4

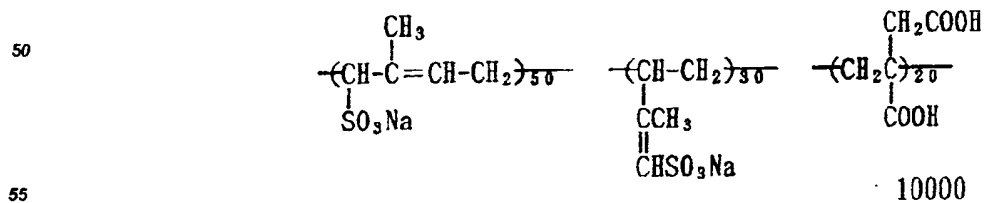


P - 5

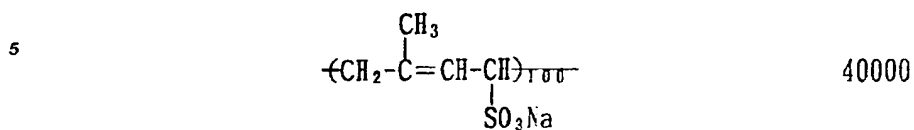


45

P - 6

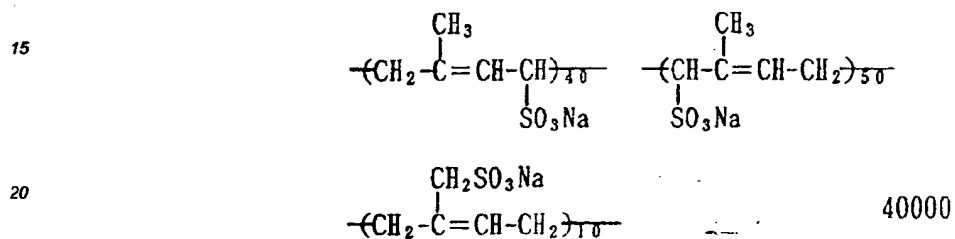


P - 7



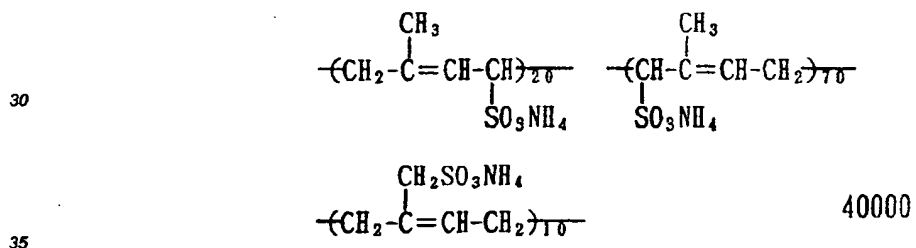
10

P - 8



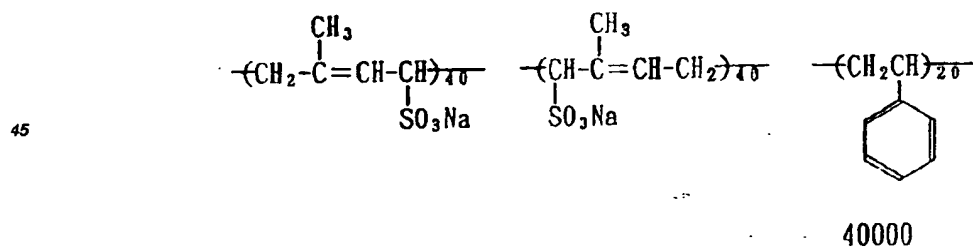
25

P - 9



40

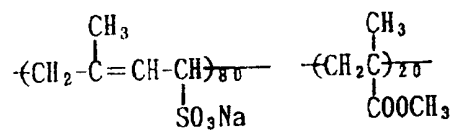
P - 10



50

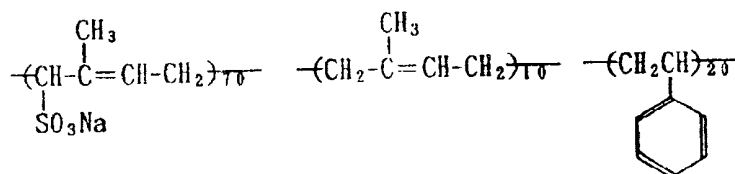
55

P - 11



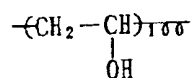
10000

P - 12



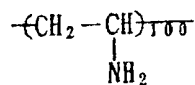
40000

P - 13



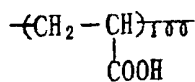
8.000

P - 14



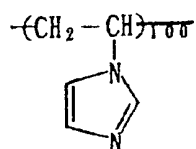
6.200

P - 15



4.800

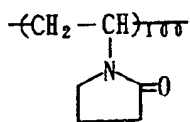
P - 16



4.700

P - 17

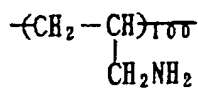
5



3.100

P - 18

10

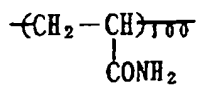


11.000

P - 19

15

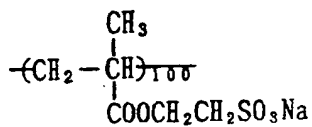
20



15.000

P - 20

25

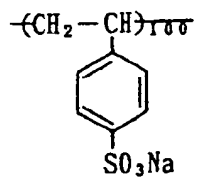


4.800

30

P - 21

35

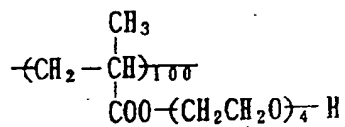


7.800

40

P - 22

45

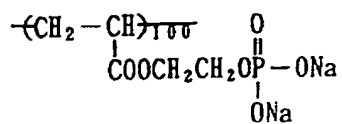


9.000

50

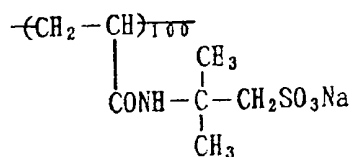
P - 23

55



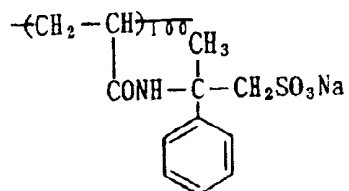
3.200

P - 24



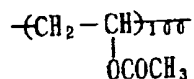
9.800

P - 25



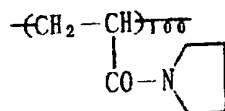
6.200

P - 26



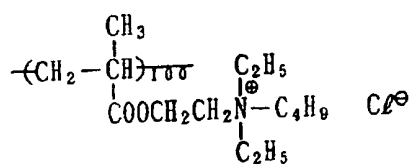
4.000

P - 27



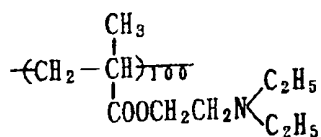
9.500

P - 28



8.200

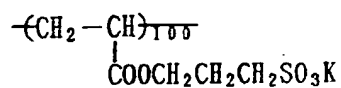
P - 29



11.000

P - 30

5

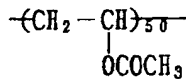
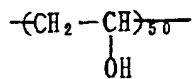


4,300

10

P - 31

15

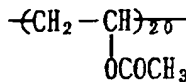
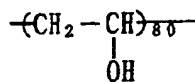


9,000

20

P - 32

25

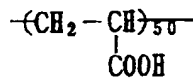
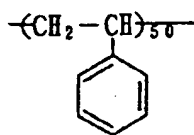


9,000

30

P - 33

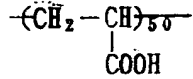
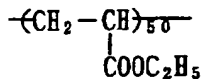
35



2,600

40

P - 34

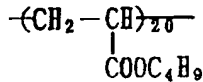
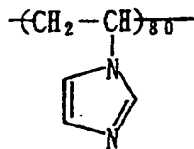


11,000

45

P - 35

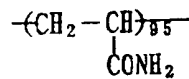
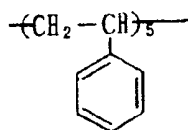
50



63,000

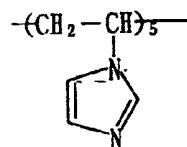
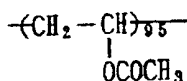
55

P - 36



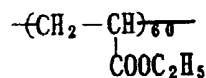
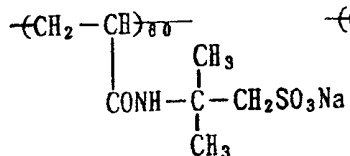
5.300

P - 37



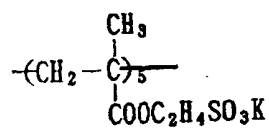
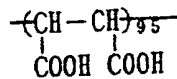
12.000

P - 38



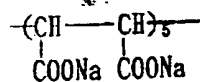
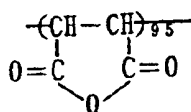
150.000

P - 39



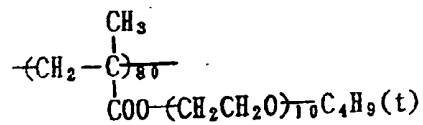
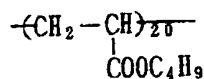
2.800

P - 40

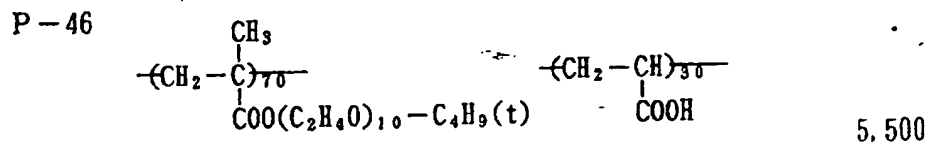
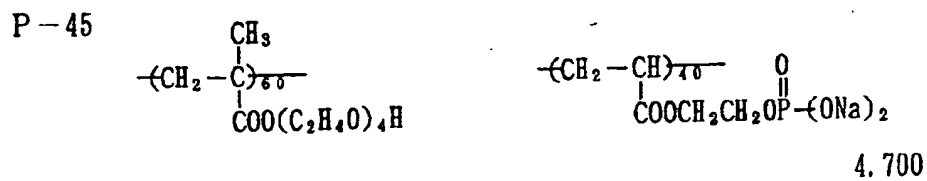
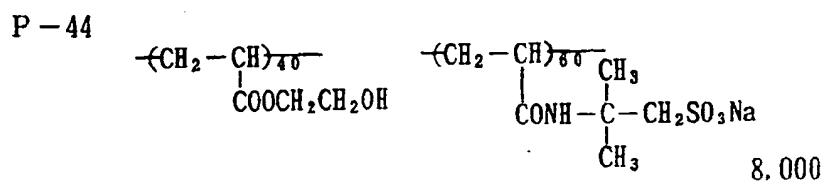
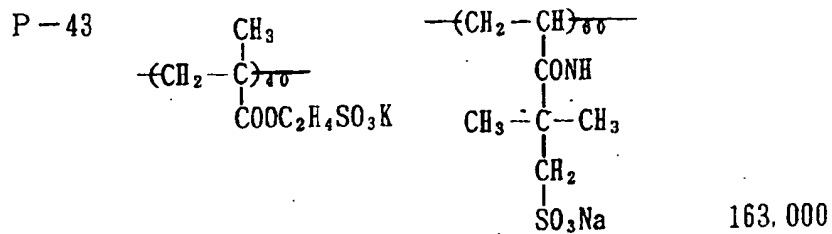
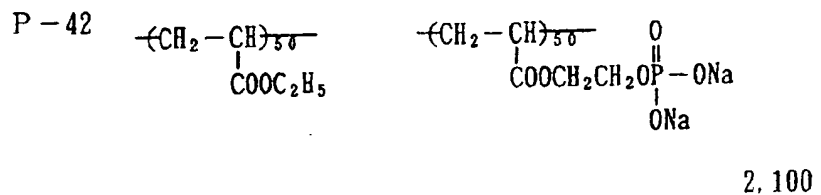



2.600

P - 41

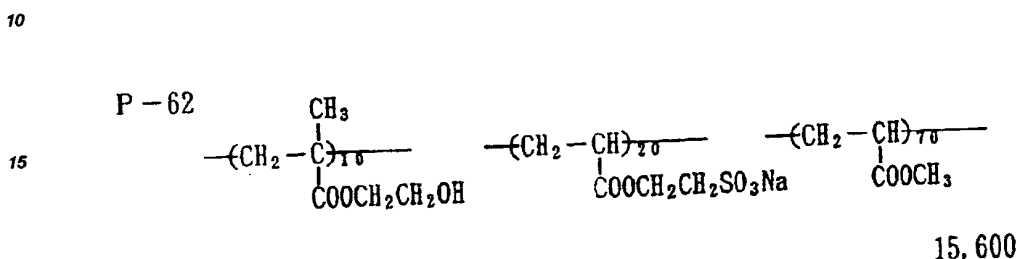
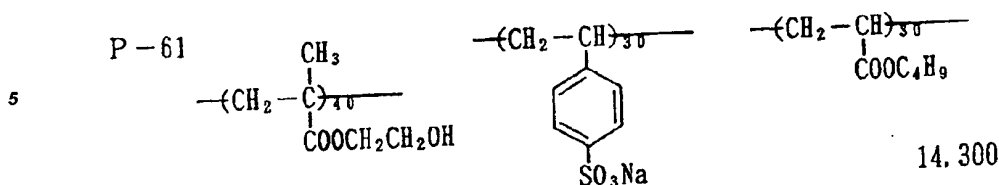


33.000



5	P-48	$\text{-(CH}_2\text{--CH)-}$ OH		$\text{-(CH}_2\text{--CH)-}$ CONH-C-CH ₂ SO ₃ Na CH ₃		3,200
10						
15		$\text{-(CH}_2\text{--C)-}$ CH ₃ COOCH ₂ CH ₂ OH		-(A)-		
20	P-49	m 50	n 50	$\text{-(CH}_2\text{--CH)-}$ COOH		7,300
25	P-50	40	60	$\text{-(CH}_2\text{--C)-}$ CH ₃ COOH		2,700
30						
35	P-51	60	40	$\text{-(CH}_2\text{--C)-}$ CH ₃ COOCH ₂ CH ₂ SO ₃ Na		4,800
40	P-52	50	50	$\text{-(CH}_2\text{--CH)-}$  SO ₃ Na		11,500
45						
50	P-53	60	40	$\text{-(CH}_2\text{--CH)-}$ COOCH ₂ CH ₂ OP(=O)(ONa) ₂		8,700
55						

5	P-54	40	60	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \\ \text{CONH---C---CH}_2\text{SO}_3\text{Na} \\ \\ \text{CH}_3 \end{array}$	5,300
10	P-55	50	50	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \\ \text{CONH---C---CH}_2\text{SO}_3\text{Na} \\ \\ \text{C}_6\text{H}_5 \end{array}$	7,900
15					
20	P-56	50	50	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---} \\ \\ \text{COOCH}_2\text{CH}_2\text{SO}_3\text{Na} \end{array}$	4,900
25					
30	P-57	50	50	$\begin{array}{c} \text{---}(\text{CH}\text{---CH})\text{---} \\ \qquad \\ \text{COOH} \text{ COOH} \end{array}$	2,800
35	P-58			$\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{CH}_2\text{---C})_{50}\text{---} \\ \\ \text{COO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{CH}_2\text{---C})_{50}\text{---} \\ \\ \text{COOCH}_2\text{CH}_2\text{SO}_3\text{Na} \end{array}$
40					6,300
45	P-59			$\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{CH}_2\text{---C})_{50}\text{---} \\ \\ \text{COO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H} \end{array}$	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})_{50}\text{---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{SO}_3\text{Na} \end{array}$
50					10,500
55	P-60			$\begin{array}{c} \text{CH}_3 \\ \\ \text{---}(\text{CH}_2\text{---C})_{50}\text{---} \\ \\ \text{COO}(\text{CH}_2\text{CH}_2\text{O})_8\text{H} \end{array}$	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})_{50}\text{---} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{SO}_3\text{Na} \end{array}$
					7,200



20

Examples of the natural water-soluble polymer includes preferably lignin, starch, pullulan, cellulose, dextran, dextrin, glycogen, alginic acid, gelatin, collagen, guar gum, gum arabic, laminarin, lichenine, nigellon and their derivatives. As derivatives of these natural water-soluble polymers there may be preferably used those sulfonated, carboxylated, phosphated, sulfoalkylenated, carboxyalkylenated, alkyl-phosphated and salts thereof, and more preferably glucose, gelatin, dextran, cellulose and their derivatives.

25

The polymer latex used in the invention can be produced easily by any one of various methods, such as by emulsion polymerization and redispersing a polymer that has been obtained in the emulsion polymerization, solution polymerization or block polymerization process.

30

In the emulsion polymerization process, water is used as a dispersion medium, and a monomer in an amount of 10 to 50% by weight of water, a polymerization initiator in an amount of 0.05 to 5% by weight of the monomer and a dispersing agent in an amount of 0.1 to 20% by weight of the monomer are used to be subjected to polymerization reaction at about 30 to 100°C, preferably at 60 to 90°C, with stirring over a period of 3 to 8 hours, whereby the polymer latex can be obtained. The concentration of the monomer, amount of the polymerization initiator, the reaction temperature, and the duration of the reaction may be broadly, easily changed.

35

Examples of the initiator include water-soluble peroxides such as potassium peroxide, ammonium peroxide; water-soluble azo compounds such as 2,2'-azobis-(2-amidinopropane)-hydrochloride.

Examples of the dispersing agent include water-soluble polymers, anionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants. These may be used alone or in combination, and preferably in combination of a water-soluble polymer with a nonionic surfactant or with an anionic surfactant.

40

In the solution polymerization, generally in an appropriate solvent such as ethanol, methanol or water, a mixture of monomers in appropriate concentrations, normally a mixture of monomers in amounts not more than 40% by weight, preferably 10 to 25% by weight of the solvent, is heated at an appropriate temperature, e.g., at 40 to 120°C, preferably 50 to 100°C, in the presence of a polymerization initiator, such as benzoyl peroxide, azobisisobutyronitrile or ammonium peroxide, to thereby effect the copolymerization of the monomers. After that, the reaction mixture is poured in a medium which does not dissolve the produced polymer to thereby sediment the product, and then the sedimented product is dried, whereby the unreacted components are removed.

45

Subsequently, the obtained product is dissolved in a solvent capable of solving the copolymer but insoluble in water, such as ethyl acetate or butanol, and then vigorously dispersed in the presence of a dispersing agent, such as a surfactant or a water-soluble polymer, and then the solvent is distilled off to thereby obtain an objective polymer latex.

50

The glass transition point Tg of the polymer to form the polymer latex used in the invention is preferably not higher than 60°C, and more preferably not higher than 40°C.

The Tg values of many polymers from ethylenic monomers usable in the invention are described in Brandrup et al., the 'Polymer Handbook' pp.III-139 through III-179 (1966) (Wiley & Sons). Tg (°K) of a copolymer is expressed by the following Formula:

$$Tg(\text{copolymer}) = v_1 Tg_1 + v_2 Tg_2 + \dots + vW TgW$$

wherein v₁, v₂...vW each represent the percentage by weight of each monomer, and Tg₁, Tg₂...TgW each represent the Tg(°K) of the homopolymer of each monomer in a copolymer.

A Tg value calculated according to the above formula has a precision of $\pm 5^{\circ}\text{C}$.

Synthetic methods of the polymer latex used in the invention are described in detail in U.S. Patent Nos. 2,852,386, 2,853,457, 3,411,911, 3,411,912 and 4,197,127, Belgian Patent Nos. 688,882, 691,360 and 712,823, JP E.P. No. 5331/1970, JP O.P.I. Nos. 18540/1985, 130217/1976, 137831/1983 and 50240/1980.

The polymer latex of the invention has an average particle size of preferably 0.5 to 300nm, and more preferably 30 to 250nm. In the invention, the average particle size means number average of particle sizes.

Measurement of the average particle size of the polymer latex of the invention may be made according to the electron-microscopic photography method, described in the 'Polymer Latex Chemistry' (Kobunshi Kanko Kai, 1973).

The molecular weight of the polymer latex used in the invention, although not restricted, is preferably from 1,000 to 1,000,000, and more preferably 2,000 to 500,000 in terms of the weight average molecular weight.

The polymer latex of the invention may, either as it is or in the state of being dispersed in water, be incorporated into photographic component layers, preferably into emulsion layers. As for the polymer latex content of the layer, it is preferably added in an amount of 5 to 70% by weight of the binder of the photographic component layer; i.e., an emulsion layer or another hydrophilic colloid layer. The polymer latex may be added to any photographic component layer regardless of whether it is a light-sensitive or non-light-sensitive hydrophilic colloid layer.

The polymer latex of the invention includes also functional polymers such as polymer couplers or polymer UV absorbing agents which are added in the form of latexes.

The following are synthesis examples of the polymer latex, but the invention is not limited thereto.

Synthesis example 1: Synthese of Lx-1

Three hundred and fifty milliliters of water were put in a 1,000ml four-neck flask equipped with a stirrer, a thermometer, a dropping funnel, a nitrogen conduction pipe and a flux condenser with its inside being deoxidized by conducting nitrogen gas thereinto, and was heated until the inside temperature reached 80°C , and to this were added 4.5g of a surfactant Sf-15 as a dispersing agent, 0.45g of ammonium persulfate as a polymerization initiator, and then added dropwise 90g of ethylhexyl acrylate for about an hour through the dropping funnel. After completion of the dropwise addition, the reaction was still continued over a period of 5 hours, and then the unreacted monomer moiety was removed by steam distillation. After-ward, the product was cooled and then its pH was adjusted to 6 with ammonia water, whereby a polymer latex having an average particle size of 150nm was obtained.

Synthesis example 2: Synthesis of Lx-2

Three hundred and fifty milliliters of water were put in a 1,000ml four-neck flask equipped with a stirrer, a thermometer, a dropping funnel, a nitrogen conduction tube and a flux condenser with its inside being deoxidized by conducting nitrogen gas thereinto and was heated until the inside temperature reached 80°C , and to this were added 4.5g of water-soluble polymer P-12 for the invention as a dispersing agent, 0.45g of ammonium persulfate as a polymerization initiator, and then dropwise added 90g of ethylhexyl acrylate for about an hour through the dropping funnel. After completion of the dropwise addition, the reaction was still continued over a period of 4 hours, the unreacted monomer moiety was removed by steam distillation. afterward, the product was cooled and its pH was adjusted to 6 with ammonia water, whereby an objective polymer latex having an average particle size of 200nm was obtained.

Synthesis example 3: Synthesis of Lx-10

Two hundred milliliters of dioxane were put in a 500ml three-neck flask with its inside being deoxidized by conducting nitrogen gas thereinto, and later to this were added 15g of isononyl acrylate, 35g of cyclohexyl acrylate and then 1.2g of dimethyl azobisisobutyrate as a polymerization initiator to have their reaction continue for 6 hours at 60°C . After completion of the reaction, the reaction liquid was poured in 3 liters of distilled water with vigorously stirring, whereby white crystals were obtained.

The white crystals were filtered, dried, and then dissolved in 100ml of ethyl acetate. This solution was added with vigorously stirring to 500ml of distilled water containing 2g of Sf-19, and then the ethyl acetate was removed, whereby an objective polymer latex having an average particle size of 180nm was obtained.

Synthesis example 4: Synthesis of comparative Latex L.

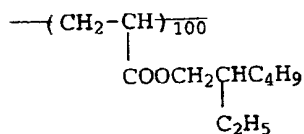
To a solution of 0.05kg of KMDS (sodium dextran sulfate, produced by Meito Ind. Co.) and 0.05kg of ammonium persulfate dissolved in 40 liters of water, with stirring at 81°C under a nitrogen atmospheric condition, was added spending an hour a mixture of 4.51kg of n-butyl acrylate, 5.49kg of styrene and 0.1kg of acrylic acid, and after that 0.005kg of ammonium persulfate was added, and further after 1.5-hour stirring, the latex product was cooled and its pH was adjusted to 6 with ammonia water.

The obtained latex was filtered by using a GF/D filter, manufactured by Whatman Co., and water was added to make the whole liquid 50.5kg, whereby a monodisperse Latex (L) having an average particle size of 250nm was obtained.

Examples of the polymer latex according to the invention are listed below, wherein each suffixed number represents the content percentage of each monomer unit, and the water solubility of each monomer is shown underneath the structural formula thereof.

Surfactant

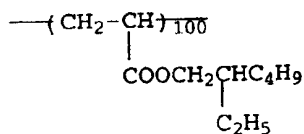
Lx-1



(0.010)

Sf-15

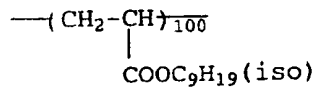
Lx-2



(0.010)

P-12

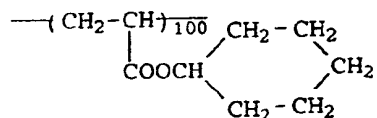
Lx-3



(0.004)

P-10

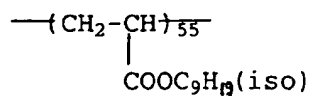
Lx-4



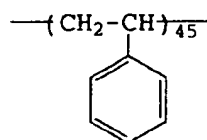
(0.010)

P-1

Lx-6



(0.004)

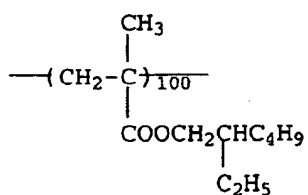


(0.030)

Sf-19

Surfactant

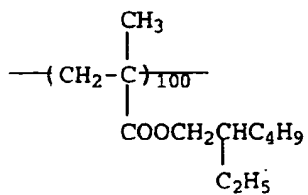
Lx-7



(0.003)

Dextransulfate

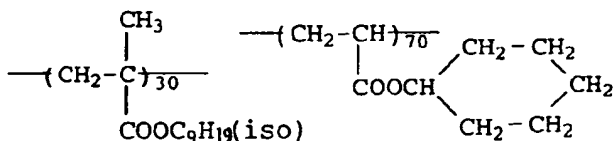
Lx-8



(0.003)

P-38

Lx-10

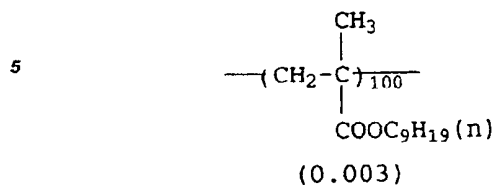


(0.003)

(0.010)

Sf-19

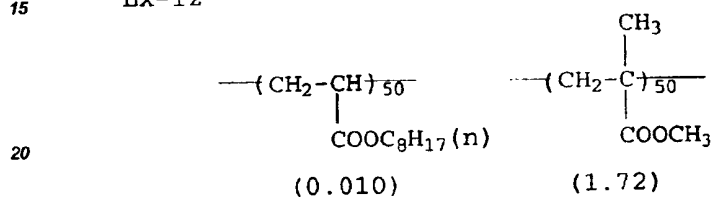
Lx-11



Sf-15

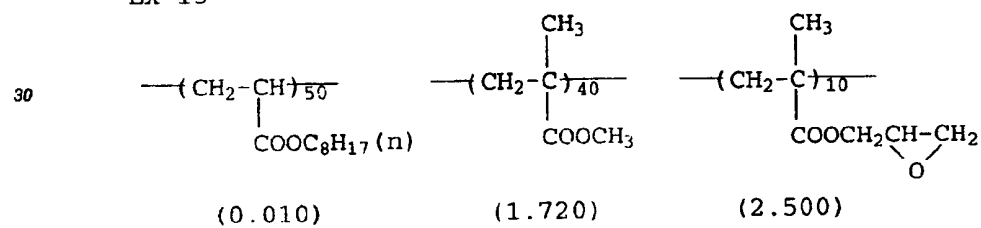
Surfactant

Lx-12



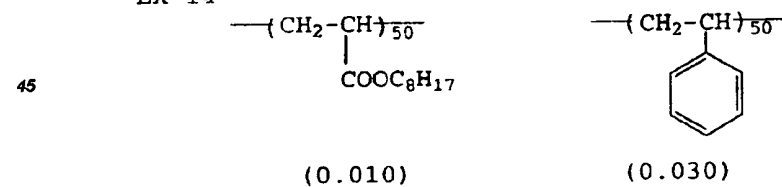
Sf-14

Lx-13



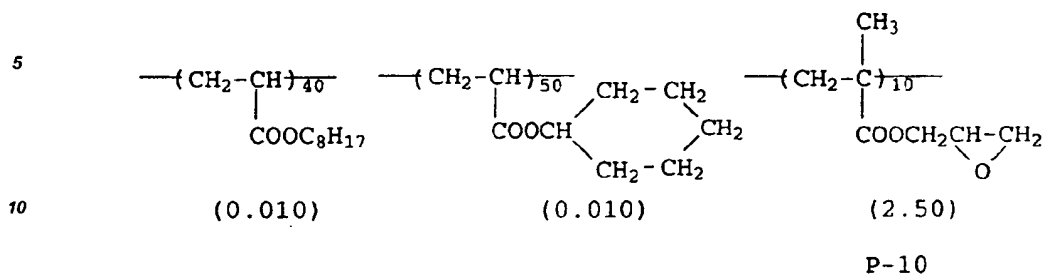
Sf-17

Lx-14



Sf-14

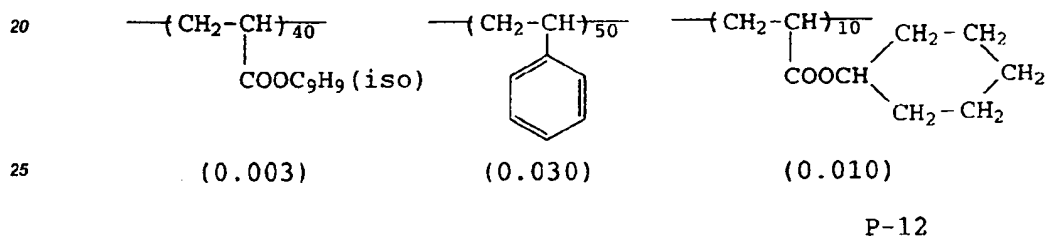
Lx-15



15

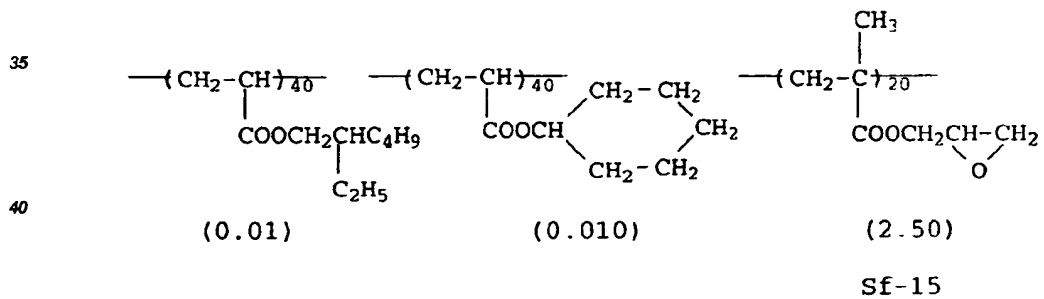
Surfactant

Lx-16



30

Lx-17

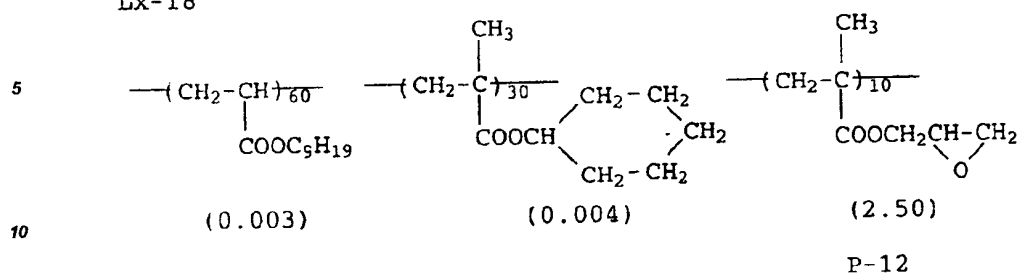


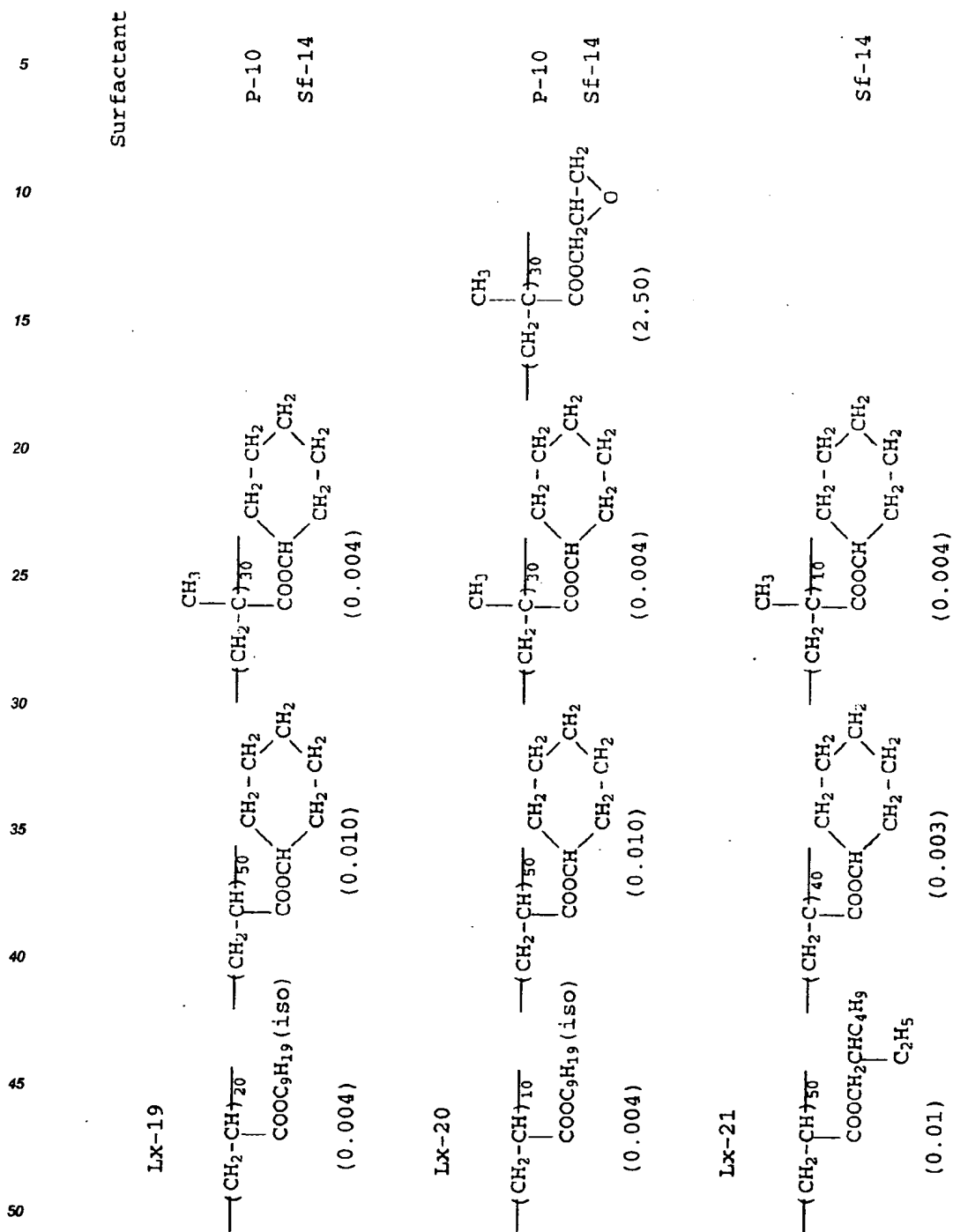
45

50

55

Lx-18





55 In the invention, the using amount of the polymer latex is preferably not less than 10% and not more than 300% by weight, and more preferably not less than 30% and not more than 200% by weight of the weight of gelatin. Further, the water-soluble polymer used in the invention accounts for preferably not less than 5% and not more than 30% by weight, and more preferably not less than 1% and not more than 15% by weight of the

polymer of the latex.

As the binder of the silver halide emulsion layer gelatin and gelatin derivatives are advantageously usable.

As the gelatin, in addition to lime-treated gelatin there may be used those acid-treated gelatin products as described in Bull. Soc. Sci. Phot. Japan No.16, p.30 (1966), and also hydrolyzed products or oxygen-decomposed products of gelatin. As the gelatin derivative there may be used those obtained by the reaction of gelatin with various compounds such as acid halides, acid anhydrides, isocyanates, bromoacetates, alkane-sulfones, vinylsulfonamides, maleimide compounds, polyalkyleneoxide or epoxy compounds; particular examples of which are described in U.S. Patent Nos. 2,614,928, 3,132,945, 3,186,846 and 3,321,553; British Patent Nos. 861,414, 1,033,189 and 1,005,784; and JP E.P. No. 26845/1967.

The silver halide for the silver halide emulsion used in the invention may be any arbitrary one of silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide and silver chloride which are used in ordinary silver halide emulsions.

The silver halide grain may be either one having a uniform silver halide composition distribution throughout the inside thereof or of the core/shell type with difference in the silver halide composition between the inside phase and the surface phase thereof, and further, it may be either one forming a latent image principally on the surface or one forming a latent image principally in the innerside thereof.

The silver halide grain for the silver halide emulsion used in the invention may be either of a regular crystal form such as a cubic, octahedral or tetradecahedral form or of an irregular crystal form such as a spherical or tabular form, but most preferably a tabular crystal form. The tabular grain herein implies one having an aspect ratio As of not less than 3.0, wherein the aspect ratio As is defined by:

$$As = R/t$$

wherein R represents the diameter of a circle equivalent in the area to the projected area of the tabular grain, and t represents the average thickness of the grain.

In such grains, those having an arbitrary {100}face/{111}-face ratio may be used. Each individual grain may take the form of a complex of these grains, or the silver halide may be a mixture of diverse crystal-form grains.

The average grain size of the silver halide (expressed in terms of the diameter of a circle equivalent in the area to projected grain image) is preferably not more than $5\mu\text{m}$, and more preferably not more than $3\mu\text{m}$.

The silver halide emulsion used in the invention may be of any grain size distribution. Either a broader grain-size distribution-emulsion called a polydisperse emulsion or a narrower grain-size distribution-emulsion called a monodisperse emulsion may be used. The monodisperse emulsion herein implies an emulsion which, when the standard deviation of its grain diameter distribution is divided by its average grain diameter, has a quotient value of not more than 0.20. The grain diameter, in the case of a spherical grain, is its diameter, while in the case of a non-spherical grain, is the diameter of a circle equivalent in the area to its projected image. The polydisperse emulsion and the monodisperse emulsion may be mixedly used.

The silver halide emulsion used in the invention may be a mixture of two or more different emulsions separately prepared.

The silver halide emulsion used in the invention may be chemically sensitized in the usual manner; i.e., the emulsion may be subjected to chemical sensitization treatment by either single use or combined use of methods of sulfur sensitization, selenium sensitization, reduction sensitization, and noble metal sensitization that uses gold compounds or other noble metal compounds.

Silver halide emulsion layers may contain dye-forming couplers to be used to form a color light-sensitive material.

That is, the silver halide photographic light-sensitive material of the invention can apply to X-ray light-sensitive materials, lith-type light-sensitive materials, black-and-white light-sensitive materials for camera use, color negative light-sensitive materials, color reversal light-sensitive materials and color photographic papers. In its application to color photographic light-sensitive materials, it can be used as either a monochromatic color light-sensitive material or a multicolor light-sensitive material. The multicolor light-sensitive material usually has dye image-forming component units separately sensitive to three primary color spectral regions, and the component units may be comprised of their respective single emulsion layers or multi-emulsion layers each consisting of plural sublayers, preferably differing in the sensitivity, sensitive separately to individual specific spectral regions, and may also have other layers such as filter layers, intermediate protective layers and a subbing layer.

Including the image-forming layers, the layers of the light-sensitive material can be coated in various orders as known to those skilled in the art.

For example, coating may be made from the support side in the order of a subbing layer, antihalation layer, cyan color-forming red-sensitive layer, intermediate layer, magenta color-forming green-sensitive layer, intermediate layer, yellow color-forming blue-sensitive layer and protective layer, and the latex in the invention can be incorporated into each of the above layers. The color-forming layers each may be of a high/low-sensitivity

double-layer construction.

To make a typical multicolor light-sensitive material a reality, it needs to comprise a support having thereon a cyan dye image-forming component comprised of a red-sensitive silver halide emulsion layer containing a cyan dye-forming coupler, a magenta dye image-forming component comprised of a green-sensitive silver halide emulsion layer containing a magenta dye-forming coupler and a yellow dye image-forming component comprised of a blue-sensitive silver halide emulsion layer containing a yellow dye-forming coupler, along with other non-light-sensitive layers.

For the multicolor light-sensitive material, suitably usable examples of the yellow coupler include open-chain keto-methylene compounds such as pivaloyl-acetanilide-type and benzoyl-acetanilide-type yellow couplers.

Useful examples of the magenta coupler include 5-pyrazolone couplers, pyrazolobenzimidazole couplers, pyrazoloazole couplers such as pyrazolotriazole couplers, and open-chain acylacetone nitrile couplers.

Useful examples of the cyan coupler includes naphthol couplers and phenol couplers.

In order to improve the photographic characteristics of the color light-sensitive material, a colorless dye-forming coupler called a competing coupler may also be incorporated.

The silver halide emulsion layers may, in addition to the above couplers, also contain a DIR compound capable of releasing a development accelerator or a precursor thereof, such as diffusible DIR compound, a timing DIR compound, or a hydroquinone derivative for preventing the layers from undesirable fogging or staining due to the aerial oxidation of a developing agent.

Particular examples of these compounds used in the color photographic light-sensitive material are described in Research Disclosure 17643 (1978) p.25 'VII Color Materials.'

EXAMPLES

EXAMPLE-1

On one side of a subbed polyethylene terephthalate support of 100 μ m in thickness were coated a backing layer with coated weight of gelatin: 2.0g/m², using the following backing layer coating liquid, and a backing protective layer with coated weight of gelatin: 1.5g/m², using the following backing protective layer coating liquid, and on the opposite subbed side of the support were coated an emulsion layer with coated weight of gelatin: 2.0g/m², and an emulsion protective layer with coated weight of gelatin: 1.0g/m², using the following silver halide light-sensitive material coating liquid, in the 4-layer simultaneous coating manner, and then dried to thereby prepare light-sensitive material Samples 101 through 117.

Preparation of backing layer coating liquid

To 36g of gelatin, after being swelled in water and heated to be dissolved, were added an aqueous solution of dyes 1.6g of Compound C-1, 310mg of Compound C-2 and 1.9mg of Compound C-3, 11 ml of an aqueous 20% saponin solution, 5g of Compound C-4 as a physical property adjusting agent, and a methanol solution of 63mg of Compound C-5.

To the above liquid were added 800mg of water-soluble styrene-maleic acid copolymer for viscosity adjustment, an aqueous citric acid solution for adjusting pH to 5.4, 1.5g of a reaction product of polyglycerol and epichlorohydrin, 44mg of glyoxal, and water to make the whole 960ml, whereby a backing layer coating liquid was prepared.

Preparation of backing layer's protective layer coating liquid

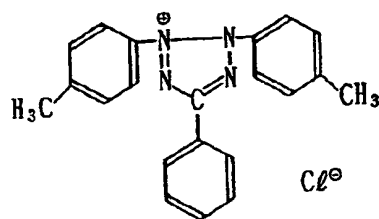
Fifty grams of gelatin were swelled in water and heated to be dissolved, and then to this were added 340mg of sodium 2-sulfonate-(2-ethylhexyl)-succinate (Sf-20), 3.4g of sodium chloride and 1.1g of glyoxal, and further added polymethyl methacrylate spherical particles, as a matting agent, having an average particle size of 4 μ m so as to have a coating weight of 40mg/m², and finally water was added to make the whole one liter, whereby a protective layer coating liquid was prepared.

Preparation of silver halide emulsion coating liquid

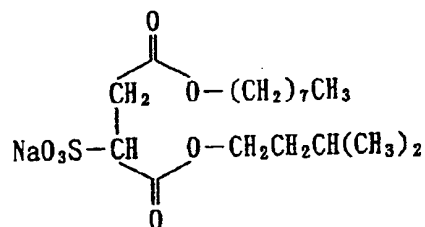
After adding 9mg of Compound (A) to the following emulsion, its pH was adjusted to 6.5 with use of a 0.5N sodium hydroxide solution. Next, to the emulsion were added 360mg of Compound T, 5ml/mol AgX of an aqueous 20% saponin solution, 180mg of sodium dodecylbenzene sulfonate, 80mg of 5-methylbenzotriazole,

60mg of Compound M, 280mg of a styrene-maleic acid copolymer water-soluble polymer as a thickener, and a compound of the invention described in Table 1 in the described order, and then water was added to make the whole 475 ml, whereby a silver halide emulsion coating liquid was prepared.

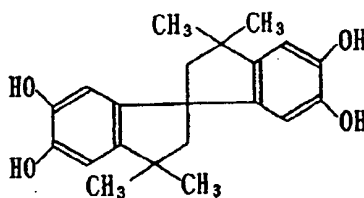
Compound T



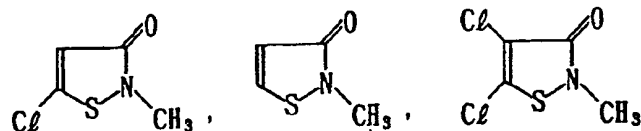
Compound Z



Compound M

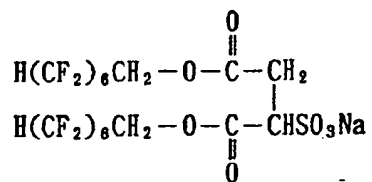


Compound A A mixture of

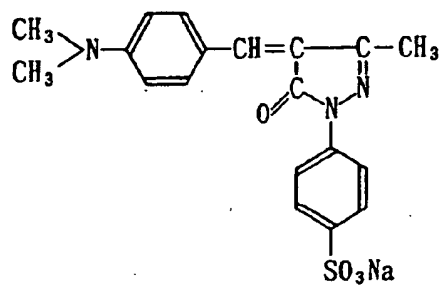


(component A) (component B) (component C)
A:B:C = 50:46:4 (molar ratio)

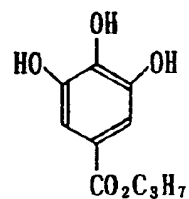
Compound Y



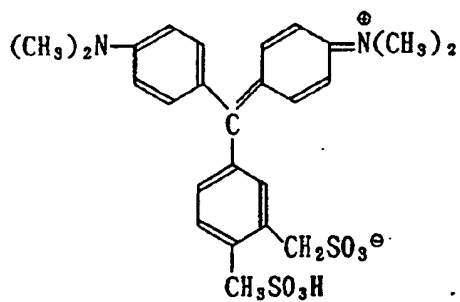
Compound N



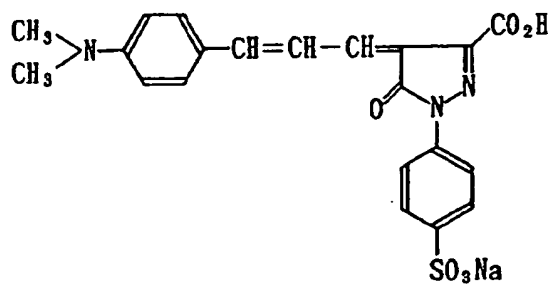
Compound D



Compound C-1



Compound C-2

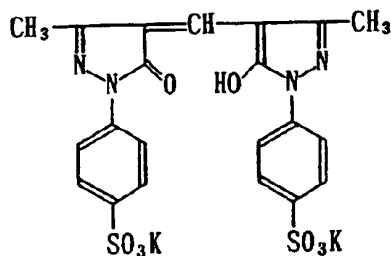


Compound C-3

5

10

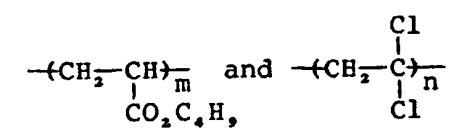
15



Compound C-4 Copolymer latex of

20

25



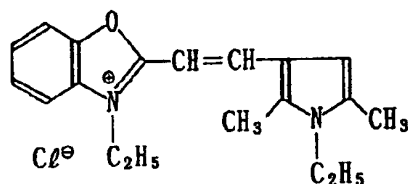
m:n = 1:1 (ratio by weight)

30

Compound C-5

35

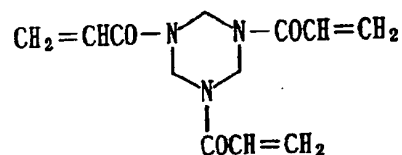
40



45

Hardener H-1

50

55 Preparation of emulsion

A silver chlorobromide emulsion having a silver bromide content of 2 mol% was prepared as follows:
An aqueous solution containing potassium pentabromorhodium in an amount of 23.9mg per 60g of silver

nitrate, sodium chloride and potassium bromide and an aqueous solution of silver nitrate were added spending 25 minutes at 40°C in a double-jet method to an aqueous gelatin solution with stirring, thereby preparing a silver chlorobromide emulsion having an average grain size of 0.20µm.

5 The above-obtained emulsion, after adding 200mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene as a stabilizer thereto, was washed for desalting.

The emulsion, after adding 20 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene thereto, was subjected to sulfur sensitization. After that, gelatin was added, 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added as a stabilizer, and water was added to make the whole 260ml to thereby complete the emulsion.

10

Preparation of emulsion protective layer coating liquid

15 Gelatin was swelled in water and dissolved at 40°C, to this were added an aqueous 1% Compound Z solution as a coating aid, an aqueous 1% solution of Compound Sf-20, Compound C as a filter dye and Compound D in the described order, and then citric acid was used to adjust pH of the mixture to 6.0. A matting agent (amorphous silica having a particle diameter of 4.0µm), Hardener H-1 and further a compound of the invention, as shown in Table 1, were added thereto, whereby an emulsion protective layer coating liquid was prepared.

20 The obtained samples were each exposed through a sensitometric stepwedge to white light and then processed in the following procedure, and on the other hand the same samples, remaining unexposed, were processed likewise, and thus two kinds of processed samples, exposed and unexposed, were prepared.

Processing conditions:

Processing step	Temperature (°C)	Time (sec.)
25 Developing	34	15
Fixing	34	15
30 Washing	Normal temperature	10
Drying	40	9

Developer solution

35

Composition A:

40 Water	150 ml
Disodium ethylenediaminetetraacetate	2 g
Diethylene glycol	50 g
45 Potassium sulfite (55%w/v solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
50 5-Methylbenzotriazole	200 mg

55

1-Phenyl-5-mercaptotetrazole 30 mg
 Potassium hydroxide amount necessary to adjust pH to 10.9
 Potassium bromide 4.5g

Composition B:

Water	3 ml
Diethylene glycol	50 g
Disodium ethylenediaminetetraacetate	25 ml
Acetic acid (90%w/w solution)	0.3ml
5-Nitroindazole	110 mg
1-Phenyl-3-pyrazolidone	500 mg

Before use, the above compositions A and B were dissolved in the order given in 500 milliliters of water, and water was added to make the whole one liter.

Fixer solutionComposition A:

Ammonium thiosulfate (72.5%w/w solution)	230 ml
Sodium sulfite	9.5g
Sodium acetate, trihydrated	15.9g
Boric acid	6.7g
Sodium citrate, dihydrated	2 g
Acetic acid (90%w/v solution)	8.1 ml

Composition B:

Water 17 ml
 Sulfuric acid (50%w/w solution) 5.8g
 Aluminum sulfate (8.1%w/w sol in Al₂O₃, equivalent)
 26.5g

Before use, the above compositions A and B were dissolved in the order given in 500 ml of water, and water was added to make the whole one liter. This fixer solution had pH of about 4.3.

The above %w/w stands for (% weight)/(weight), and %w/v for (% weight)/(volume). The obtained Samples 101 to 117 were evaluated according to the following methods. The results are shown in Table 1.

Evaluation methods

Haze:

- 5 Each unexposed sample processed was measured with respect to its haze by use of a turbidimeter Model T-2600DA, manufactured by Tokyo Denshoku Co., and the haze is shown in percentage.

The result of coating:

- 10 The number of lumps present within a 100cm²-wide surface area of each unexposed sample processed in the foregoing processing procedure was counted visually.

Photographic sensitivity:

- 15 The exposed samples processed in the foregoing procedure were each subjected to sensitivity measurement with use of a sensitometer KS-1, manufactured by KONICA Corp. The sensitivity of each sample is a reciprocal of the exposure amount necessary to give a density of fog + 0.7, and is indicated as a speed relative to the immediate speed of the control sample set at 100.

20 Scratch:

- After being developed, fixed and washed in the foregoing processing, each sample was again put in the developer solution at a designated temperature to be subjected to a scratch test, wherein the sample's surface kept immersed therein was scratched by a weighted metallic needle to find the minimum needle weight necessary to damage the surface (scratch resistance).
- 25

 The results are shown in Table 1.

30

35

40

45

50

55

Table 1

5	Sample No.	Polymer latex		Haze %	Number of lumps/100 cm ²	Photo-graphic speed	Scratch g
		EM layer mg/m ²	Protective layer mg/m ²				
		LX-2					
	101 (Inv.)	800		5	1	97	47
		LX-3					
10	102 (' ')	800		4	3	98	51
		LX-5					
	103 (' ')	800		6	2	97	48
		LX-9					
	104 (' ')	800		4	3	96	48
15		LX-10					
	105 (' ')	800		5	2	98	53
		LX-15					
	106 (' ')	800		6	4	97	50
		LX-17					
20	107 (' ')	800		5	3	98	49
		LX-19					
	108 (' ')	800	-	3	1	99	52
		LX-20					
	109 (' ')	800	-	4	3	99	54
25		LX-21					
	110 (' ')	800	-	6	4	98	53
			LX-10				
	111 (' ')		800	5	2	97	49
			LX-10				
30			500				
	112 (' ')		P-12	4	3	98	50
			300				
		LX-10	LX-10				
	113 (' ')	500	500	4	3	99	51
35		LX-18					
	114 (' ')	800		5	4	98	48
		LX-18	LX-13				
	115 (' ')	500	500	3	3	98	52
		LX-L					
40	116 (Comp.)	800		18	14	84	25
		LX-M					
	117 (' ')	800		6	13	88	29
			LX-L				
	118 (' ')		800	17	16	82	25
45		LX-L	LX-L				
	119 (' ')	500	500	15	23	81	21
	120 (' ')			4	1	100	22

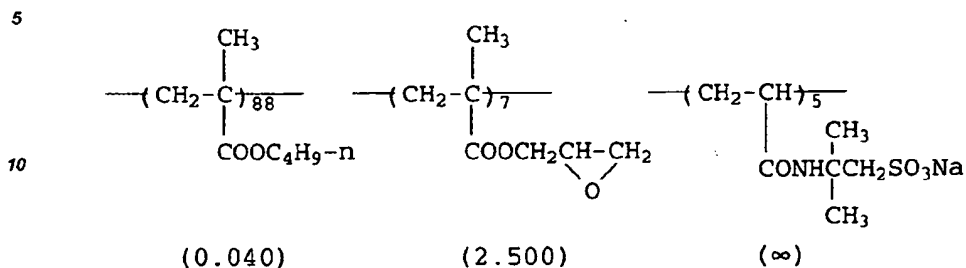
50 Comparative latex: LX-M

Latex LX-M was prepared in the same manner as in LX-L except that the following monomers and surfactant Sf-19 were used.

55

Surfactant

Sf-19



15 From the results shown in Table 1, it is apparent that the samples which contain the compound of the invention are excellent in the photographic speed as well as in the layer physical properties including the haze (little turbidity, good transparency), the result of coating (having few or no comet coating defects due to laumps) and scratch resistance.

20 EXAMPLE-2

One side (obverse side) of a cellulose triacetate film support was subbed, and on the other side (nonsubbed reverse side) of the same support were coated the following backing layers in order from the support side.

25 Backing layer 1

The following backing layer 1 coating liquid was coated at a rate of 20 ml/m², and then dried at 80°C in 5 minutes.

30

Aluminasol AS-100 (product of Nissan Chem. Ind.,Co.)	40 g
Acetone	500 ml
Methanol	400 ml
Dimethyl formamide	100 ml

35

40 Backing layer 2

On the above backing layer 1 the following backing layer 2 coating liquid was coated at a rate of 20 ml/m² and dried at 80°C in 5 minutes.

45

Diacetyl cellulose	1.0g
SiO ₂ fine particles (average particle size: 3.0μm)	0.02g
Acetone	500 ml
Ethyl acetate	500 ml

50

Backing layer 3

55 On the backing layer 2 the following backing layer 3 coating liquid was coated at a rate of 20 ml/m², and dried at 90°C in 5 minutes.

EP 0 615 158 A1

Carnauba wax	10 g
Polyoxyethylene-lauryl ether	1 g
Water	950 ml
Methanol	750 ml
Propylene glycol	50 ml

Subsequently, on the nonbacking obverse side (EM side) of the support were coated the following compositions-having layers in order from the support side, whereby a multilayer color photographic light-sensitive material samples were prepared. In the following layers, the amounts of the components are given in terms of grams per square meter of the sample. The amount of silver halide and colloidal silver is described as that of silver.

Layer 1: Antihalation layer (HC)	
Black colloidal layer	0.15
UV absorbent UV-1	0.20
Colored cyan coupler CC-1	0.02
High-boiling solvent Oil-1	0.20
High-boiling solvent Oil-2	0.20
Gelatin	1.6

Layer 2: Intermediate layer (IL-1)	
Gelatin	1.3

Layer 3: Low-speed red-sensitive emulsion layer (R-L)

Silver iodobromide emulsion (average grain diameter:

0.3 μ m, average iodide content: 2.0 mol%) 0.4

Silver iodobromide emulsion (average grain diameter:

0.4 μ m, average iodide content: 8.0 mol%) 0.3

Sensitizing dye S-1 3.2×10^{-4} mol/mol Ag

" S-2 3.2×10^{-4} mol/mol Ag

" S-3 0.2×10^{-4} mol/mol Ag

Cyan coupler C-11 0.50

" C-12 0.13

	Colored cyan coupler CC-1	0.07
	DIR compound D-1	0.006
5	" D-2	0.01
	High-boiling solvent Oil-1	0.55
10	Additive SC-1	0.003
	Gelatin	1.0

15	<u>Layer 4: High-speed red-sensitive emulsion layer (R-H)</u>	
	Silver iodobromide emulsion (average grain diameter: 0.7 μ m, average iodide content: 7.5 mol%)	0.9
	Sensitizing dye S-1	1.7x10 ⁻⁴ mol/mol Ag
20	Sensitizing dye S-2	1.6x10 ⁻⁴ mol/mol Ag
	Sensitizing dye S-3	0.1x10 ⁻⁴ mol/mol Ag
	Cyan coupler C-2	0.23
25	Colored cyan coupler CC-1	0.03
	DIR compound D-2	0.02
	High-boiling solvent Oil-1	0.25
30	Additive SC-1	0.003
	Gelatin	1.0

35	<u>Layer 5: Intermediate layer (IL-2)</u>	
	Gelatin	0.8

40

Layer 6: Low-speed green-sensitive emulsion layer (G-L)

45	Silver iodobromide emulsion (average grain diameter: 0.4 μ m, average iodide content: 8.0 mol%)	0.6
	Silver iodobromide emulsion (average grain diameter: 0.3 μ m, average iodide content: 2.0 mol%)	0.2

55

	Sensitizing dye S-4	6.7×10^{-4} mol/mol Ag
	" S-5	0.8×10^{-4} mol/mol Ag
5	Magenta coupler M-1	0.17
	" M-2	0.43
10	Colored magenta coupler CM-1	0.10
	DIR compound D-3	0.02
	High-boiling solvent Oil-2	0.70
15	Additive SC-1	0.003
	Gelatin	1.0

20	<u>Layer 7: High-speed green-sensitive emulsion layer (G-H)</u>	
	Silver iodobromide emulsion (average grain diameter: 0.7 μ m, average iodide content 7.5 mol%)	0.9
25	Sensitizing dye S-6	1.1×10^{-4} mol/mol Ag
	Sensitizing dye S-7	2.0×10^{-4} mol/mol Ag
	Sensitizing dye S-8	0.3×10^{-4} mol/mol Ag
30	Magenta coupler M-1	0.03
	Magenta coupler M-2	0.13
	Colored magenta coupler CM-1	0.04
35	DIR compound D-3	0.004
	High-boiling solvent Oil-2	0.35
	Gelatin	1.0

40

Layer 8: Yellow filter layer (YC)

	Yellow colloidal silver	0.1
45	Additive HS-1	0.07
	Additive HS-2	0.07
50	High-boiling solvent Oil-2	0.15
	Gelatin	1.0

55

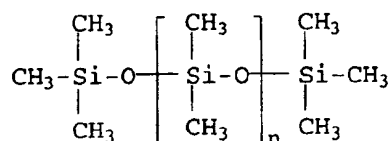
Layer 9: Low-speed blue-sensitive emulsion layer (B-L)		
5	Silver iodobromide emulsion (average grain diameter: 0.3 μ m, average iodide content 2.0 mol%)	0.25
	Silver iodobromide emulsion (average grain diameter: 0.4 μ m, average iodide content 8.0 mol%)	0.25
	Sensitizing dye S-9	5.8x10 ⁻⁴ mol/mol Ag
10	Yellow coupler Y-1	0.60
	Yellow coupler Y-2	0.32
	DIR compound D-1	0.003
15	DIR compound D-2	0.006
	High-boiling solvent Oil-2	0.18
	Gelatin	1.3
20	Layer 10: High-speed blue-sensitive emulsion layer (B-H)	
	Silver iodobromide emulsion (average grain diameter: 0.8 μ m, average iodide content 8.5 mol%)	0.5
25	Sensitizing dye S-10	3.0x10 ⁻⁴ mol/mol Ag
	Sensitizing dye S-11	1.2x10 ⁻⁴ mol/mol Ag
	Yellow coupler Y-1	0.18
30	Yellow coupler Y-2	0.10
	High-boiling solvent Oil-2	0.05
35	Gelatin	1.0

Layer 11: First protective layer (PRO-1)

40	Silver bromide (average grain diameter: 0.08 μ m)	0.3
	UV absorbent UV-1	0.07
45	'' UV-2	0.1
	Additive HS-1	0.2
50	Additive HS-2	0.1
	High-boiling solvent Oil-1	0.07
	'' Oil-3	0.07
55	Gelatin	0.8

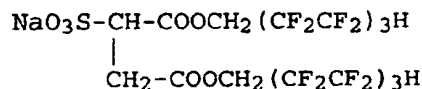
Layer 12: Second protective layer (PRO-2)	
Compound A	0.04
Compound B	0.004
Polymethyl methacrylate (average particle size: 3 μ m)	0.02
Copolymer of methyl methacrylate:ethyl methacrylate: methacrylic acid = 3:3:4 by weight (average particle size: 3 μ m)	0.13
Gelatin	0.5

Compound A



weight average molecular weight = 30,000

Compound B



The silver iodobromide emulsion used in Layer 10 was prepared in the following manner:

A silver iodobromide emulsion was prepared according to a double-jet method with monodisperse silver iodobromide grains having a silver iodide content of 2 mol% and an average grain diameter of 0.33 μ m used as seed crystals.

To Solution <G-1>, with stirring under conditions of its temperature, pAg and pH being kept at 7.0°C, 7.8 and 7.0, respectively, was added the seed emulsion in an amount equivalent to 0.34 mol.

High-iodide-core phase formation

After that, Solutions <H-1> and <S-1>, at a flow rate ratio of 1:1, were added at an accelerated flow rate (final flow rate: 3.6 times the initial), spending 86 minutes.

Low-iodide-shell phase formation

Subsequently, to the reaction system, with its pAg and pH being kept at 10.1 and 6.0, respectively, were added Solutions <H-2> and <S-2> at a flow rate ratio of 1:1 and at an accelerated flow rate (final flow rate: 5.2 times the initial), spending 65 minutes.

Controls of pAg and pH during the grain formation were carried out by using an aqueous potassium bromide solution and an aqueous 56% acetic acid solution. After the formation of grains, the grains were subjected to washing treatment according to the usual flocculation method, then redispersed by adding gelatin thereto, and then the pH and pAg thereof were adjusted at 40°C to 5.8 and 8.06, respectively.

The obtained emulsion was a monodisperse emulsion of octahedral silver iodobromide grains having a silver iodide content of 8.5 mol%, an average grain diameter of 0.80 μ m and a grain size distribution broadness of 12.4%.

Solution <G-1>:	
Osein gelatin	100.0g
Compound [I], 10% by weight methanol solution	25.0ml
28% aqueous ammonia solution	440.0ml
56% aqueous acetic acid solution	660.0ml
Water to make	5000.0ml

Solution <H-1>:	
Osein gelatin	82.4g
Potassium bromide	151.6g
Potassium iodide	90.0g
Water to make	1030.5ml

Solution <S-1>:	
Silver nitrate	309.2g
28% aqueous ammonia solution	Necessary amount
Water to make	1030.5ml

Solution <H-2>:

Osein gelatin	302.1g
Potassium bromide	770.0g
Potassium iodide	33.2g
Water to make	3776.8ml

Solution <S-2>:	
Silver nitrate	1130.0g
28% aqueous ammonia solution	Necessary amount
Water to make	3776.8ml

In the above, the 'necessary amount' of the ammonia solution means the amount thereof necessary for making an ammoniacal silver nitrate solution.

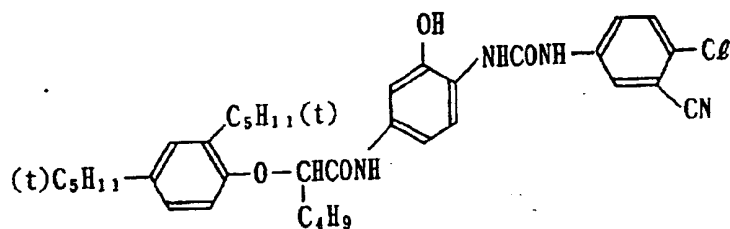
Emulsions different in the average grain diameter and silver iodide content used in the layers other than Layer 10 were prepared in the same manner as in the above emulsion except that the average grain diameter of seed crystals, temperature, pAg, pH, flow rate, adding period of time and halide composition were varied.

The thus obtained emulsions were all core/shell-type monodisperse emulsions having a grain size distribution broadness of not more than 20%. Each of the emulsions was subjected optimal chemical ripening treat-

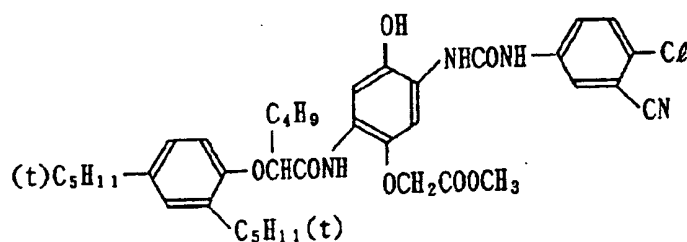
ment in the presence of sodium thiosulfate, chloroauric acid and ammonium thiocyanate, and then to it were added sensitizing dyes and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene-1-phenyl-5-mercaptotetrazole.

Besides, the above light-sensitive material samples each contain Compounds Su-1 and Su-2, Stabilizer ST-1, Antifoggants AF-1 and AF-2 (weight average molecular weights 10000 and 1100000), Dyes Al-1 and Al-2, and 4.9mg/m² of Compound DI-1.

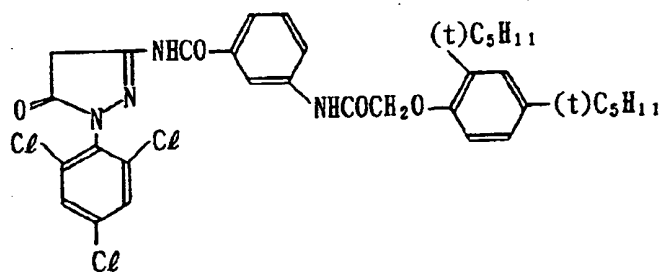
C-11



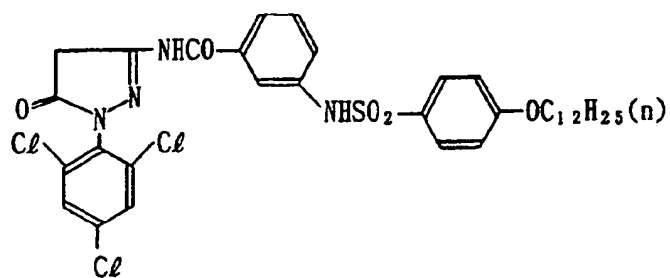
C-12



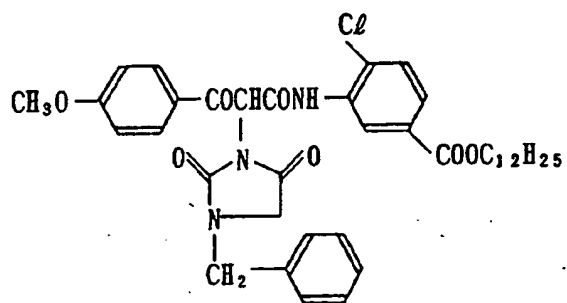
M-1



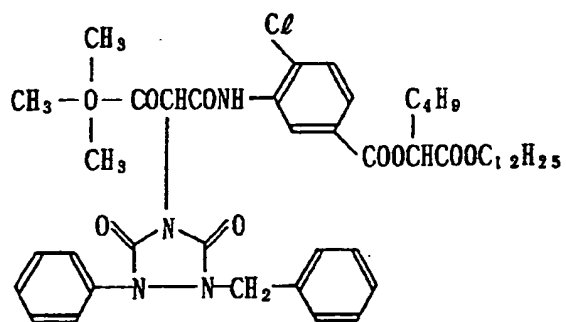
M-2



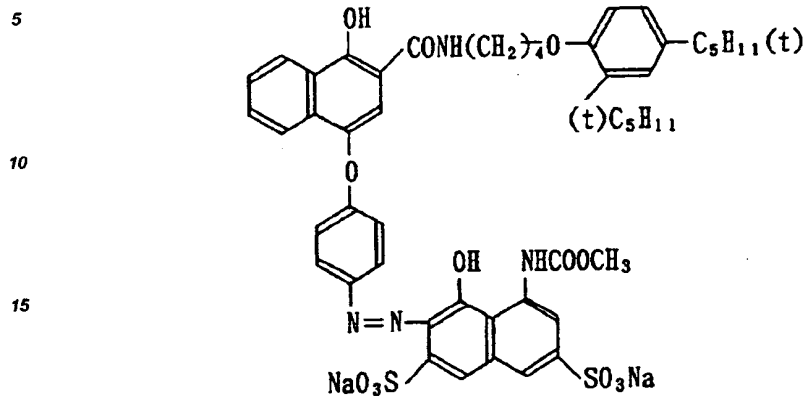
Y-1



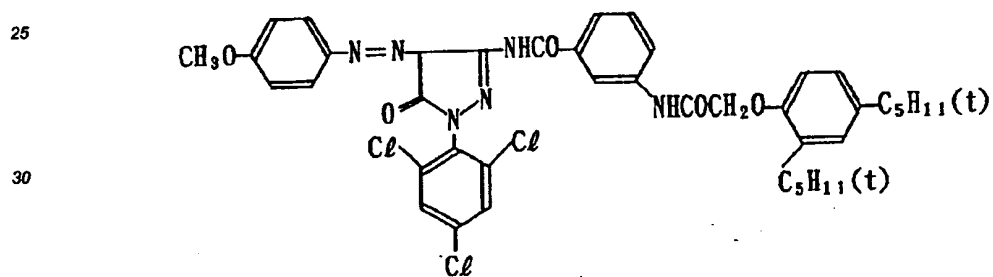
Y-2



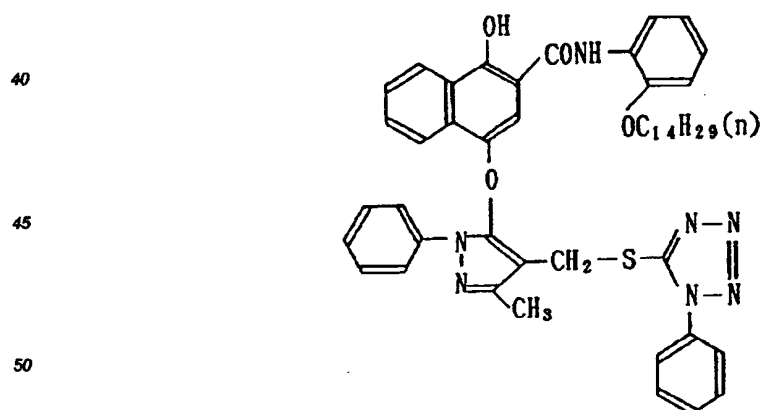
CC-1



CM-1



D-1

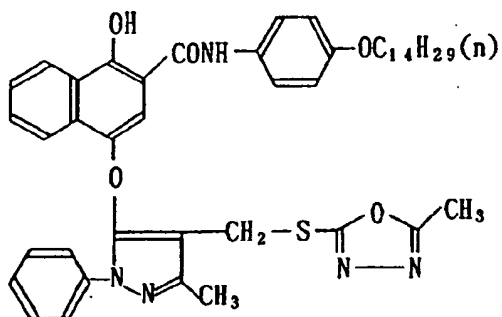


D-2

5

10

15



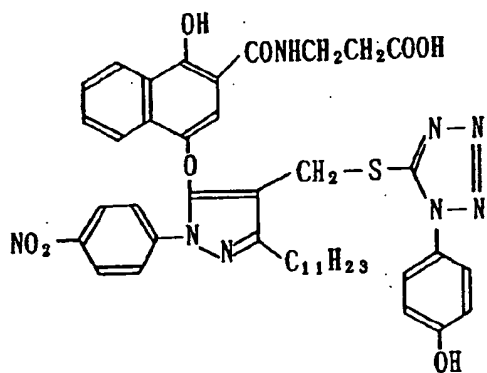
D-3

20

25

30

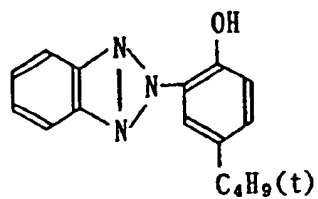
35



UV-1

40

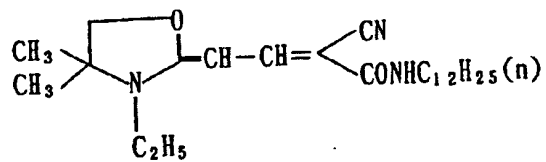
45



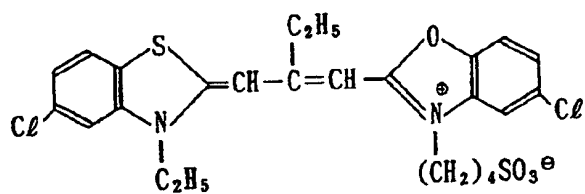
50

55

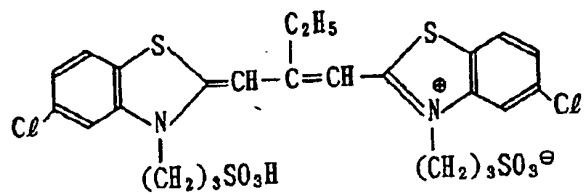
UV-2



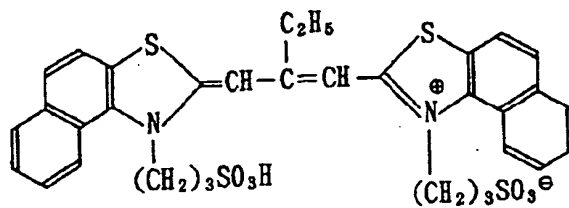
S-1



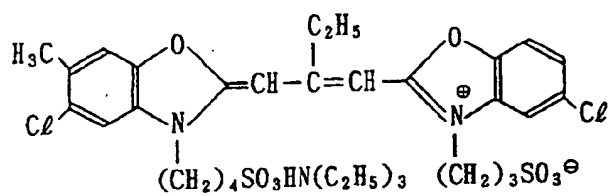
S-2



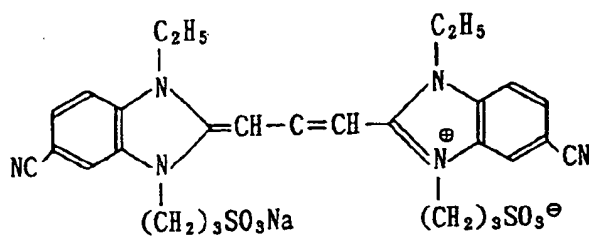
S-3



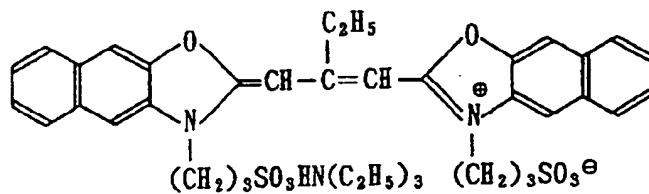
S-4



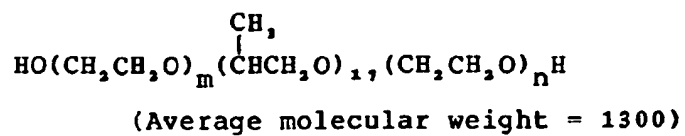
S-5



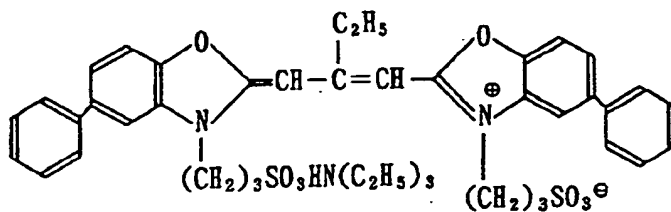
S-6



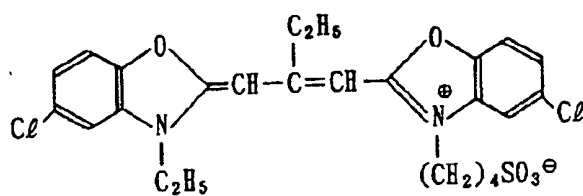
Compound [1]



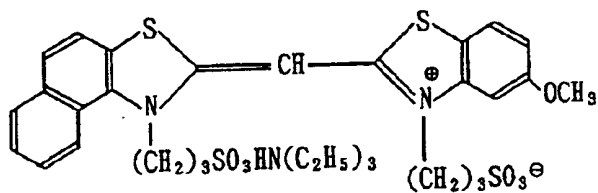
S-7



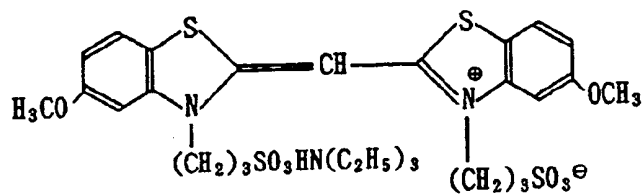
S-8



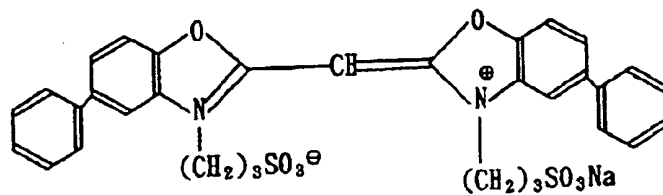
S-9

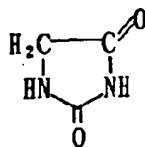


S-10

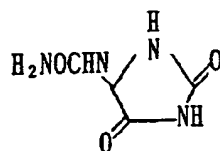


S-11





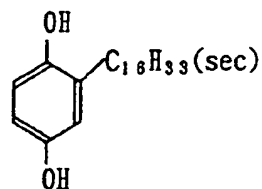
HS-2



Sc-2

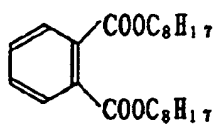
CC1=C(C(=C(C=C1)O)O)C2=CC=CC=C2C3=CC=CC=C3

and

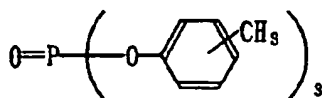


(Mixing ratio: 2:3)

Oil-1

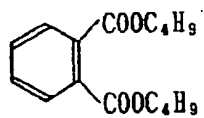


Oil-2



Oil-3

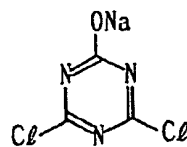
5



10

H-2

15

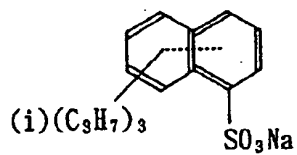


20

H-3 (CH₂=CHSO₂CH₂)₂ O
Su-1

25

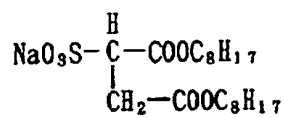
30



35

Su-2

40



45

50

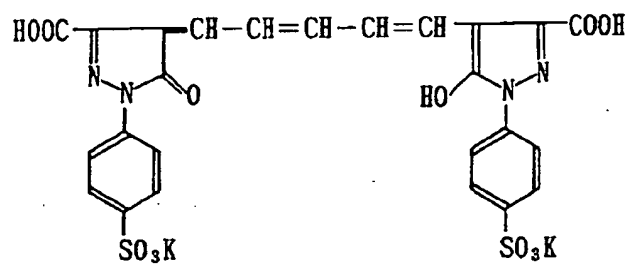
55

AI-1

5

10

15

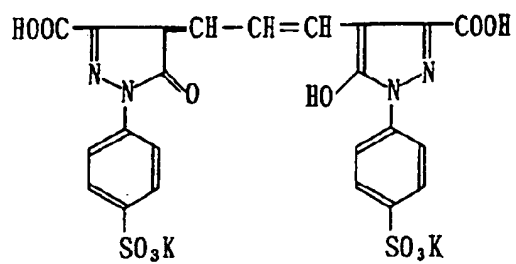


AI-2

20

25

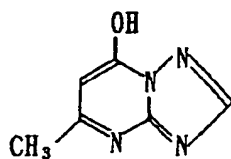
30



ST-1

35

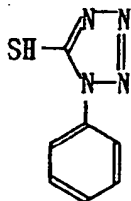
40



AF-1

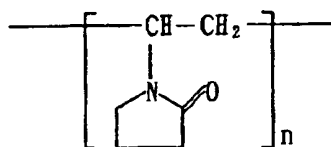
45

50

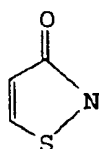


55

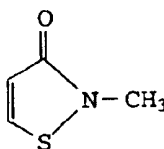
AF-2



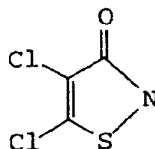
DI-1: Mixture of the following compounds



(A)



(B)



(C)

A:B:C = 50:46:4 in mol ratio

Measurement of pressure fog

Samples for the pressure fog measurement were prepared in the darkroom and were cut to 35mm x 111mm size pieces. Each piece was put in a rollfilm cartridge having an inside diameter of 22mm and loaded in a camera FT-1, manufactured by KONICA Corp. The sample remaining loaded in the camera was subjected to a one-

full-day accelerated aging test at 23°C/80%RH. Each light-sensitive material sample was wound up, processed in the following steps, and then evaluated for pressure fog.

Both the spotted fog's yellow density and the density of the fog-free area at the leading end of each sample were measured with a microdensitometer to find the density difference ΔD between them.

Antistatic characteristic test:

Each unexposed light-sensitive material sample was placed with its protective layer side down on a rubber sheet; had its backing side squeezed with a rubber roller; and then peeled apart from the rubber sheet to cause static electricity to be discharged. The sample was then processed to make its discharged marks into visible static marks, and the degree of the marks generation was rated on the following 5-step evaluation basis. Those classified as A and B are acceptable for practical use.

A: No static marks at all

B: Slight static marks

C: Considerable static marks

D: Conspicuous static marks

E: Overall static marks

Each of the above prepared samples was exposed through an optical wedge to white light, and then processed as follows:

	<u>Processing step</u>	<u>Time</u>	<u>Temperature</u>	<u>Repl. amt.</u> [*]
5	Color developing	3 min. 15 sec.	38°C	780 ml
	Bleaching	45 sec.	38°C	150 ml
	Fixing	1 min. 30 sec.	38°C	830 ml
10	Stabilizing**	60 sec.	38°C	830 ml
	Drying	1 min.	55°C	-
15	* The replenishing amount is a value per m ² of the light-sensitive material.			

** The stabilizing was made in tribath cascade system.

Color developer

25	Water	800 ml
	Potassium carbonate	30 g
	Sodium hydrogencarbonate	2.5g
30	Potassium sulfite	3.0g
	Sodium bromide	1.3g
	Potassium iodide	1.2mg
35	Hydroxylamine sulfate	2.5g
	Sodium chloride	0.6g
	4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.5 g
40	Diethylenetriaminepentaacetic acid	3.0g
	Potassium hydroxide	1.2g

Water to make one liter.

Adjust pH to 10.06 with potassium hydroxide or 20% sulfuric acid.

EP 0 615 158 A1

Color developer replenisher

	Water	800 ml
5	Potassium carbonate	35 g
	Sodium hydrogencarbonate	3 g
10	Potassium sulfite	5 g
	Sodium bromide	0.4g
	Hydroxylamine sulfate	3.1g
15	4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)- aniline sulfate	6.3g
	Potassium hydroxide	2 g
20	Diethylenetriaminepentaacetic acid	3 g

Water to make one liter.

25 Adjust pH to 10.18 with potassium hydroxide or 20% sulfuric acid.

Bleaching solution

30	Water	700 ml
	Ferric ammonium 1,3-diaminopropanetetraacetate	175 g
	Disodium ethylenediaminetetraacetate	2 g
35	Sodium nitrate	50 g
	Ammonium bromide	150 g
	Glacial acetic acid	40 g

40 Water to make one liter.

Adjust pH to 4.4 with ammonia water or glacial acetic acid.

Bleaching solution replenisher

45	Water	700 ml
	Ferric ammonium 1,3-diaminopropanetetraacetate	180 g
	Disodium ethylenediaminetetraacetate	2 g
50	Sodium bromide	50 g
	Ammonium bromide	200 g
	Glacial acetic acid	56 g

55 Adjust pH to 4.0 with ammonia water or glacial acetic acid, and add water to make the whole one liter.

Fixing solution

5

10

Water	800 ml
Ammonium thiosulfate	150 g
Ammonium thiocyanate	120 g
Sodium sulfite	15 g
Disodium ethylenediaminetetraacetate	2 g

Adjust pH to 6.2 with acetic acid or ammonia water, and add water to make the whole one liter.

Fixer replenisher

15

20

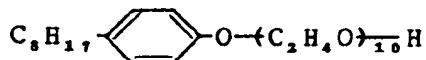
Water	800 ml
Ammonium thiosulfate	180 g
Ammonium thiocyanate	150 g
Sodium sulfite	20 g
Disodium ethylenediaminetetraacetate	2 g

25

Adjust pH to 6.5 with acetic acid or ammonia water, and add water to make the whole one liter.

Stabilizing solution and stabilizer replenisher

30



2.0g

Dimethylolurea

0.5g

Hexamethylenetetramine

0.2g

35

1,2-benzisothiazoline-3-one

0.1g

Cyclohexane (L-77, produced by UCC)

0.1g

40

Ammonia water

0.5ml

Water to make one liter.

Adjust pH to 8.5 with ammonia water or 50% sulfuric acid.

The results are shown in Table 2.

45

50

55

Table 2

Sample No.	Polymer latex of inv.			Pressure fog	Result of coating (number of lumps/100cm ²)	Photographic speed	Scratch (g)
	added layer	added amt (mg/m ²)					
201 (Comp.)	-	-		0.21	0	100	22
Comparative							
202 (Comp.)	Layer 12	Lx-L	200	0.13	18	86	20
203 (Inv.)	Layer 12	Lx-10	200	0.07	2	98	35
204 (Inv.)	Layer 12	Lx-15	200	0.08	2	99	36
205 (Inv.)	Layer 12	Lx-17	200	0.06	4	97	40
206 (Inv.)	Layers 3, 6, 9	Lx-10	200	0.05	5	96	43
207 (Inv.)	Layers 3, 6, 9	Lx-17	200	0.04	4	95	37
208 (Inv.)	Layers 2, 5	Lx-10	200	0.04	4	97	35

As is apparent from Table 2, the samples containing the compound of the invention are excellent in respect of being free from comet-shaped defects due to lumps in coating as well as in the photographic characteristics (fog, speed) and scratch resistance.

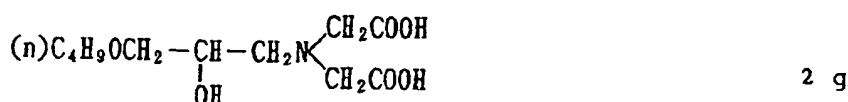
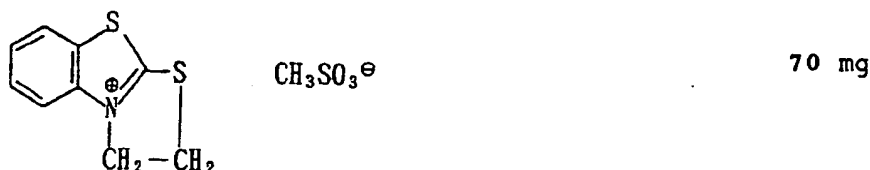
EXAMPLE-3

On the subbed side of a blue-tinted polyethylene terephthalate film support of 180μm in thickness were simultaneously coated four layers - three emulsion layers (coating weight of gelatin: 2.0g/m²) and one emulsion protective layer (coating weight of gelatin: 1.2g/m²) - by using the following emulsion layer coating liquids and emulsion protective layer coating liquid, whereby light-sensitive material Samples 301 to 313 were prepared.

Preparation of silver halide emulsion coating liquids

The following emulsion at 55°C was subjected to goldsulfur sensitization treatment by adding ammonium thiocyanate and hypo thereto. After completion of the sensitization 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added. In the final stage, the emulsion was divided into parts to add separately appropriate sensitizing dyes thereto to thereby prepare different color sensitivity-having emulsion coating liquids. To each emulsion coating liquid were added the following additives in the following amounts per mol of silver:

t-Butyl-catechol	400 ml
Polyvinyl pyrrolidone (Mw = 10000)	1.0g
Styrene-maleic anhydride copolymer	2.5g
Trimethylol propane	10 g
Diethylene glycol	5 g
Nitrophenyl-triphenylphosphonium chloride	50 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	15 mg



1,1-dimethylol-1-bromo-1-nitromethane	10 mg
---------------------------------------	-------

Further the hydrophobic particles of the invention shown in Table 3 were added, whereby the emulsion coating liquids were prepared.

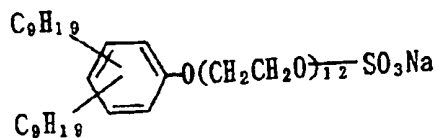
Preparation of emulsion

A silver iodobromide monodisperse cubic crystal grain emulsion having an average grain diameter of 0.3 μm and a silver iodide content of 2 mol% was obtained under controlled conditions of a temperature of 60°C, pAg=8 and pH=2.0 by a double-jet process. The reacting solution was desalted by the use of Demol N, a product of KAO-Ailas Co., and a magnesium sulfate solution. The thus obtained flocks of emulsion was redispersed in a gelatin solution. Subsequently, 8.5 liters of a proctive gelatin solution kept at 40°C containing ammonia as needed were added to the emulsion, and pH of it was adjusted to 9.7 with use of acetic acid. To this solution as a mother liquid was added a 3.2 N ammoniacal silver ion aqueous solution by a double-jet method, during which pH and pAg were controlled to 7.3 and 9.7, respectively, to form a phase having a silver iodide content of 3.5 mol%, and then the grain was grown until it comes to 95% size under conditions of pH changed from 9 to 8 with pAg kept at 9.0. Afterward, a potassium bromide solution was added through a nozzle spending 8 minutes, pAg was lowered to 11.0, and the mixing was completed 3 minutes after the addition potassium bromide. The obtained emulsion was of an average grain diameter of 0.55 μm , and the silver iodide content of the overall grain thereof was about 2.2 mol%. Next, in order to remove the excessive soluble salts from the reaction liquid, the liquid was kept at 40°C and to it were added 5g/mol Ag of naphthalene sulfonate-formalin condensate oligomer and 8g/mol Ag of MgSO_4 with stirring for 5 minutes, and then the liquid was allowed to stand for a while. After that, the supernatant was decanted off to make the volume of the liquid 200 ml per mol of Ag. Then, pure water at 40°C in an amount of 1.8 liter/mol Ag was added and the liquid was stirred for 5 minutes, followed by adding 20g/mol Ag of MgSO_4 with stirring likewise and then decanting off the supernatant, thus effecting the desalting of the liquid. To the desalted liquid with stirring gelatin was added for redispersion of AgX, whereby the preparation of the emulsion was carried out.

Preparation of emulsion protective layer coating liquid

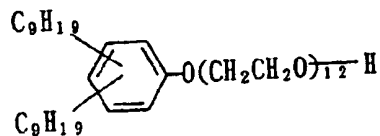
The following compounds were added (in amounts per g of gelatin):

5



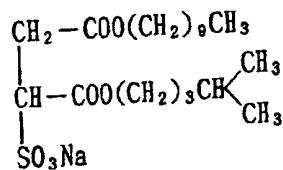
10 mg

10



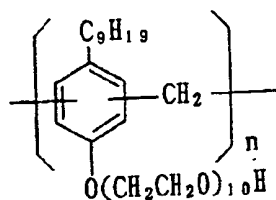
2 mg

15



7 mg

20



a mixture of those
whose number of units
n is 2 to 5

15 mg

30

35 Further, 7 mg of a matting agent comprising polymethyl methacrylate having an average particle size of 5 μm , 70 mg of colloidal silica having an average particle size of 0.013 μm , the compound of the invention shown in Table 3, 8 mg of glyoxal and 6 mg of formalin were added to thereby prepare a protective layer coating liquid.

The thus obtained samples were evaluated in the same manner as in Example 1.

The results are shown in Table 3.

40

45

50

55

Table 3

Sample No.	Emulsion layer (mg/m ²)	EM protective layer (mg/m ²)	Haze (%)	Number of lumps/100 cm ²	Photographic speed	Scratch (g)	Static marks
301 (Inv.)	Lx-10(500)		4	2	98	49	A
302 (Inv.)	Lx-15(500)		3	1	99	52	A
303 (Inv.)	Lx-17(500)		4	2	97	48	A
304 (Inv.)	Lx-19(500)		3	1	99	54	A
305 (Inv.)	Lx-20(500)		3	2	99	52	A
306 (Inv.)	Lx-21(500)		3	3	98	50	A
307 (Inv.)	--	Lx-10(500)	5	3	97	49	B
308 (Inv.)	--	Lx(15(500)	5	1	98	47	A
309 (Inv.)	Lx-15(500)	Lx-15(500)	4	2	97	48	A
310 (Comp.)	L(500) for comparison	--	9	10	88	29	D
311 (Comp.)	--	L(500) for comparison	13	15	89	30	E
312 (Comp.)	L(500) for comparison	L(500) for comparison	15	23	88	25	E
313 (Comp.)	--		3	0	100	27	A

As is apparent from Table 3, the samples containing the compound of the invention are excellent in respect of being free from comet-shaped defects due to lumps in coating as well as in the photographic characteristics (speed, pressure fog), scratch resistance and antistatic characteristics.

Claims

1. A silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer and optionally a hydrophilic colloid layer, wherein at least one of said silver halide emulsion layer and hydrophilic colloid layer contains a latex of polymer comprising a repeating unit derived from a monomer having a solubility in water of not higher than 0.025 % by weight at 25°C and the content of said repeating unit in said polymer is not less than 50 % by weight.
2. The light-sensitive material of claim 1, wherein said polymer comprises a repeating unit derived from an acrylic acid ester monomer having a solubility in water of not higher than 0.025 % by weight at 25°C.
3. The light-sensitive material of claim 1, wherein said polymer comprises a repeating unit derived from an acrylic acid ester monomer and a methacrylic acid ester monomer each having a solubility in water of not higher than 0.025 % by weight at 25°C.
4. The light-sensitive material of claim 1, wherein said latex comprises particles of said polymer having an average particle size of not larger than 300 nm.
5. The light-sensitive material of claim 1, wherein said polymer of latex is formed by polymerization reaction carried out in the presence of a water-soluble polymer.

6. The light-sensitive material of claim 6, wherein said polymer of latex is formed by polymerization reaction carried out in the presence of a water-soluble polymer and a surfactant.
7. The light-sensitive material of claim 1, wherein said latex is contained in said silver halide emulsion layer.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 1571

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
X	EP-A-0 358 187 (EASTMAN KODAK COMPANY) * claims; examples * ---	1-7	G03C1/053 G03C1/76 G03C1/89
X	JP-A-63 198 047 (MITSUBISHI PAPER MILLS LTD) & ChemAbs 110(14):125289x * example (2) of the table on p.3 (329) * ---	1-7	
X	EP-A-0 048 700 (MINNESOTA MINING AND MANUFACTURING COMPANY) ---	1-7	
X	PATENT ABSTRACTS OF JAPAN vol. 9, no. 101 (P-353) (1824) 2 May 1985 & JP-A-59 224 839 (KONISHIROKU SHASHIN KOGYO K.K.) 17 December 1984 * abstract * ---	1-7	
X	PATENT ABSTRACTS OF JAPAN vol. 9, no. 101 (P-353) (1824) 2 May 1985 & JP-A-59 224 838 (KONISHIROKU SHASHIN KOGYO K.K.) * abstract * ---	1-7	
X	US-A-3 495 986 (S.FRANCO ET AL) * claims; examples 9, 10 * ---	1-7	
P,X	EP-A-0 535 535 (EASTMAN KODAK COMPANY) * page 31, line 20; claims 1-11; examples 1-7 * ---	1-7	
P,X	EP-A-0 557 785 (ILFORD LIMITED) * latex 6 in table 1; claims * -----	1-7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 June 1994	Examiner Buscha, A
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, not published on, or after the filing date D: document cited in the application L: document cited for other reasons & : member of the same patent family, corresponding document	

EP 0 615 158 A1 (P. 1/1)

THIS PAGE BLANK (USPTO)